AN INNOVATIVE APPLICATION OF CHELATING AGENTS FOR EOR IN CARBONATE RESERVOIRS

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PETROLEUM ENGINEERING

May 2013

An Innovative Application of Chelating Agents for EOR in Carbonate Reservoirs

BY

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A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

Petroleum Engineering

May 2013

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

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Date

Dedicated to my beloved Home Country Egypt,

My parents

And

My Brothers

Whose Prayers and Perseverance led to this accomplishment

ACKNOWLEGMENT

Praise is to Allah, Lord of the Worlds, the most compassionate, and the most merciful who has given me the strength and patience to accomplish this degree.

I would like to express my sincere thanks to my supervising professor Dr. Mohamed A. Mahmoud. I am grateful for his assistance and guidance throughout my studies and research, I am heartily thankful to him, whose encouragement, supervision and support from the preliminary to the concluding level enabled me to develop an understanding of this subject. I wish to extend my appreciation to Dr. Hasan S. Al-Hashim and Dr. Abdullah S. Sultan for devoting their invaluable time to review my research work and evaluate its results. Their comments during the course of my studies are highly appreciated. Many thanks to the Kingdom of Saudi Arabia for providing a scholarship during my studies at King Fahd University of Petroleum & Minerals.

I wish to express my love and gratitude to my beloved family; my Parents, and my brothers, for their understanding and infinite support they have shown through my life.

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LIST OF ABBREVIATIONS

EOR	Enhanced oil recovery
EDTA	Ethylenediaminetetraacetic acid
BCA	Biodegradable Chelating Agent
HEDA	HydroxyEthyleneDiamineTriAcetic Acid
PV	Pore Volumes
Wt%	Weigh present
Na^+	Sodium ion concentration
Ca^{2+}	Calcium ion concentration
Mg^{2+}	Magnesium ion concentration
SO_4^{2-}	Sulfate ion concentration
Na_4EDTA	Tetrasodium Ethylenediamine TetraAcetate
NH_4EDTA	Tetra-ammonium Ethylenediamine TetraAcetate
IFT	Interfacial tension
MIE	Multicomponent ion exchange
OOIP	Original Oil in place
IC	Ionic Chromatography
°C	Degree Celsius
LSE	low-salinity effect
LowSal	Low salinity waterflooding
K_f	Formation Constant
S_{or}	Residual Oil saturation
M	Molar

ABSTRACT

Full Name : Khaled Zidan Abdelgawad Ibrahim

Thesis Title : An Innovative Application of Chelating Agents for EOR in Carbonate Reservoirs.

Major Field : Petroleum Engineering

Date of Degree : [May, 2013]

Despite the fact that about half of the world's proven oil reserves are present in carbonate reservoirs, its average oil recovery is lower than that from sandstone reservoirs. This has been attributed mainly to the fact that carbonate reservoirs are usually neutral to oil-wet, which hinder the waterflooding process from being efficient. Chemical enhance oil recovery (EOR) process is a tertiary method for oil recovery that has promising results for future development. It has already been implemented in different areas of the world. The success of this process return to the extensive research work in the area of rock/fluids interaction and introducing new EOR fluids for enhancing oil recovery from different reservoir rock types. The main objective of this research is to introduce a new chemical EOR method to recover more oil from carbonate reservoirs. In this study a chelating agent (High pH ethylenediaminetetraacetic acid (EDTA)) has been tested as a chemical enhanced oil recovery fluid for carbonate reservoirs. The specific objectives of this work are to study and evaluate the performance of chelating agents as an enhanced oil recovery fluid and compare it to conventional waterflooding techniques. The results of fluids study showed that chelating agents considered in this study have the ability to chelate different cations present in the injected water which stimulated the calcite formations to exchange cations with the injected solutions, and change the wettability of the rock towards more water-wet. Furthermore, chelating agents having high pH (pH> 12) have the ability to reduce the interfacial tension. Consequently this will result in higher capillary

number (The ratio of viscous to capillary forces) which is a key parameter in enhanced oil recovery (EOR) process.

ملخص الرسالة

الاسم : خالد زيدان عبد الجواد إبراهيم

عنوان الرسالة : تطبيق مبتكر للمركبات المخلبية لتحسين إستخراج النفط من الخزانات الكربونية.

التخصص : هندسة النفط

تاريخ الدرجة العلمية: مايو 2013

على الرغم من أن نصف الإحتياطى العالمى للبترول يوجد فى المكامن الكربونية فإن متوسط إستخلاص النفط من هذه المكامن الكربونية أقل بكثير منه فى حالة المكامن الرملية. يرجع هذا غالبا إلى خاصية التبلل فى المكامن الكربونية والتى يكون فيها سطح الصخرأكثر تبللا بالزيت الخام أو بنفس درجة التبلل بالماء والذى يعوق فاعلية عمليات الإزاحة بالماء فى إستخراج كميات أكبر من الزيت.

إن الطرق الكيميائية لإستخراج الزيت المعزز تعتبر المرحلة الثالثة فى العمر الإنتاجى للمكامن ولها نتائج واعدة مع التطوير المستمر فى المستقبل وقد تم تطبيقها فى أنحاء مختلفة من العالم. ويعود نجاح الطرق الكيميائية لإستخراج الزيت المعزز إلى مقدار البحث العلمى المبذول حول التاثير المتبادل بين الصخر والسوائل الموجودة فى الخزانات البترولية والتأثير الذى تسببه المواد الكيميائة التى يتم ضخها فى صخور المكامن المختلفة لتعزيز إستخلاص النفط الخام.

تهدف هذه الدراسة إلى تقديم طريقة كيميائية جديدة لتعزيز إستخراج مزيد من النفط من المكامن الكربونية. وقد قمت فى هذه الدراسة بإختبار إمكانية إستخدام المركبات العضوية المسماة بالمركبات المخلبية كطريقة مبتكرة لإستخلاص الزيت المعزز من المكامن الكربونية. كذلك تهدف هذه الدراسة إلى تقييم ودراسة أداء هذه الطريقة المقترحة فى تعزيز إنتاج النفط ومقارنته بالطرق التقليدية لإستخدام المياه فى إزاحت الزيت الخام.

وقد وجد أن المواد الكيميائية المستخدمة فى هذه الطريقة المبتكرة لتعزيز إنتاج الزيت الخام لديها القدرة على عمل روابط تشبه الكلاليب مع كتيونات الأملاح المختلفة عند إضافتها للمياه المستخدمة فى إزاحة الزيت الخام وهذا بدوره يحفز الصخر الكربونى على تبادل الكتيونات بين سطح الصخر والمحاليل التى يتم ضخها مما يؤدى إلى تغيير خاصية التبلل لسطح الصخر فى اتجاه أكثر تبللا بالماء. تتميز هذه المواد المخلبية ذات الرقم الهيدروجينى الأعلى من 12 بخاصية تقليل التوتر السطحى الذى ينتج عنه زيادة نسبة قوى اللزوجة إلى القوى الشعرية وهوما يعرف بالرقم الشعري الذى يعد عاملا مهما فى تقييم عملية تعزيز إنتاج النفط الخام.

CHAPTER 1

INTRODUCTION

Usually, only 5-30 % of original oil-in-place (OOIP) can be recovered by the reservoir initial pressure energy during the primary production period (Farouq-Ali and Stahl, 1970). As the reservoir pressure falls towards the bubble point of the oil, we should try to maintain the reservoir pressure above the bubble point to prevent the liberation of high mobility gas in the reservoir. Injection of water into the reservoir is the usual way to maintain the reservoir pressure during production. The method can be a supplement to reservoirs having natural water-drive or an expanding gas cap. The injected water will:

- Maintain the reservoir pressure above the bubble point ensuring that no gas is liberated in the reservoir and thereby maintain high relative permeability for oil
- Push the oil in front of the water towards the production well.

The waterflooding method started in 1870 (Schumacher, 1978), and was found to increase oil recovery by 40-60 % of OOIP. This stage of the oil production process is called the secondary production period. During the waterflooding period, oil production is associated with a steady increasing water-oil ratio at the production wells. After time the water-oil ratio becomes too high and the oil cannot be produced in a cost effective way but still at this stage there is about 40-60 % of OOIP left in the reservoir, mainly because of unfavorable wettability conditions,

Enhanced oil recovery (EOR; sometimes called tertiary oil recovery methods) consists of methods aimed to increase ultimate oil recovery by injecting appropriate agents not

normally present in the reservoir, such as chemicals, solvents, oxidizers and heat carriers in order to induce new mechanisms for displacing the remaining oil which is the target of EOR process.

The main EOR methods can be divided into three categories, which according to Marie (1991) consist of the following methods: chemical, miscible, and thermal methods. **Fig. 1** shows the three main types (chemical, miscible and thermal) of EOR methods according to their action on the sweep efficiency at the macroscopic scale or on the displacement efficiency at the pore scale. Each method is aimed to either:

- Increase the sweep efficiency (increase the area swept by the injected water), or
- Act at the pore scale level by increasing the microscopic displacement efficiency in areas previously swept by water, hence reducing the residual oil saturation.

Some methods can improve both the sweep efficiency at the macroscopic scale and the displacement efficiency at the pore scale at the same time such as Alkali-surfactant-polymer (ASP) flooding.

Chemical flooding is one of these processes that have been used to enhance hydrocarbon recovery aiming to extend the lifetime of oil reservoirs producing by support of waterflooding or other conventional methods, which are approaching the economical limit.

Chemical EOR are characterized by the addition of chemicals to water in order to reduce the mobility of the displacing fluid and/or to lower oil/water interfacial tension. For example surfactants use the technique of lowering oil/water IFT. High-pH alkalines are being used to produce in-situ surfactant.

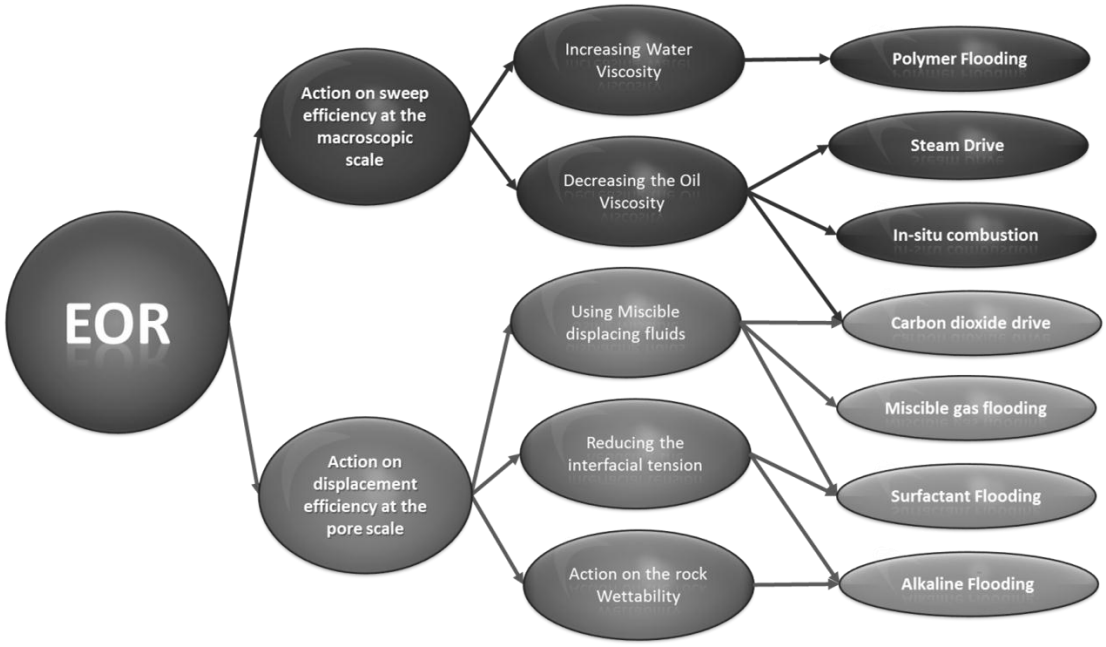


Fig. 1— The Acting mechanism of different EOR methods (Redrawn after Marie, 1991).

The new chemical EOR method combines most of the chemical methods features to increase oil recovery or in other ways reduce residual oil saturation (S_{or}) by increasing the solution pH, changing the rock surface wettability towards more water wet, and preventing the precipitation of metals sulfate in the formation by chelating the present cations in the solution.

Also High quality injection water is important in order to avoid both formation damage and scale deposition problem due to mixing of incompatible waters in the reservoir, producing wells, flow lines and surface facilities. One solution is to remove the sulfate from seawater prior to injection; this is possible by using the nanofiltration process (Hardy et al., 1994; Hardy and Simm, 1996; O'Donnell., 1996; Vu et al;, 1999 and Evans et al., 2009) but the proposed method enable us to inject the seawater as it is without any sulfate removal processes which means an effective way to reduce operating cost of EOR and Waterflooding projects.

The new method overcomes the complexity of surfactant flooding technique as it does not need too much sophisticated laboratory testing to support field project design, more over the new method is inexpensive compared to all the chemical EOR methods.

The most important advantage of the proposed method is that the injected chelating agent holds the metals present in the solution from tubular corrosion during the injection process in solution, preventing it from forming complex precipitants in the formation and reducing its permeability.

1.1 Objectives

The main objective of this work is to test the chelating agent (EDTA tetrasodium solution) as a new EOR chemical fluid to improve oil recovery from carbonate reservoirs.

The objectives will be achieved by performing core flooding tests using the EDTA chelating agent after seawater flooding at reservoir conditions. Different Chelating agent will be tested at different concentrations and it will be injected into oil-saturated limestone core plugs under reservoir conditions. The improvement of the produced oil will be compared with the conventional waterflooding process on the same cores. The specific objectives are:

1. Investigate the potential of EDTA as a new EOR chemical fluid in seawater solution through flooding process.
2. To better understand the mechanism leading to incremental oil recovery by low salinity (LowSal) waterflooding.
3. Optimize the additional recovery using different concentrations of EDTA.
4. Study the effect of different chelating agents such as EDTA, HEDTA, and BCA solutions on the seawater injection.
5. Providing the first step towards implementation of the newly proposed method on industrial scale.

1.2 Research Approach

In this study, carbonate core plugs were selected from outcrops and the following will be conducted

1. Rock characterization which includes:
    - Porosity
    - Permeability
    - Grain Density
    - Initial water saturation
2. The cores will then be aged at least for two weeks under pressure and 100^{o}C temperature.
3. Perform waterflooding using Arabian Gulf seawater till no more oil recovery followed by flooding with chelating agent solutions.
4. Repeat step 3 using fresh core sample and different concentrations of chelating agents.
5. Brine-saturated cores will be flooded with different chelating agents to study the effect of chelating agents on the injectors during pressure maintenance or secondary recovery processes.

1.3 Thesis Organization

The organization of this thesis is as follows:

Chapter 1: Presents a prelude to this research and lists the objectives of this work.

Chapter 2: Presents an overview of chemical EOR recovery methods and with the basic principle and literature review covering low salinity waterflooding, chelating agents, chelation chemistry, and degradation of EDTA chelating agent.

Chapter 3: Presents the statement of problem and the idea behind this research work in addition to an extensive review of the debating regarding the mechanism behind the increased oil recovery during low salinity waterflooding work presented in the literature and the value which our work will help in understanding the recovery mechanism. Finally motivating hints regarding the introduced EOR chemical method have been given at the end of this chapter.

Chapter 4: Presents a detailed description of the experimental program planned for this research. The experimental program consists of core samples selection and basic properties measurements in addition to the description of the core flooding experiments conducted during this study.

Chapter 5: Presents the results of all cores flooding experiments with detailed analysis, discussion and the conclusion out of the thesis work and highlights research major outcomes with recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Chemical EOR

Chemical methods have been used both to increase the macroscopic sweep efficiency and the microscopic displacement efficiency on the pore scale level. Many types of chemicals are injected to recover oil, but they generally fall within one of three groups: polymers, surfactants and alkalis. Historically, polymer injection has been applied significantly more often than the other two methods. Modern chemical floods can be highly successful at displacing remaining oil, with oil recovery in the high 90% range reported in the laboratory and the field.

Long-chain polymers are injected along with water or other flooding agents to improve the viscosity ratio, thereby decreasing viscous fingering. Polymer injection is used both for near-well conformance control and for formation sweep control. Polymer-gel treatment and polymer flooding have been used to shut-off high-permeability zones in the reservoir and to increase the swept areas in the reservoirs due to increased water viscosity respectively. Both methods are used with the purpose of increasing the macroscopic sweep efficiency.

Surfactant flooding mainly acts by decreasing the oil-water interfacial tension. Surfactant chemicals are medium- to long-chain molecules that have both a hydrophilic and a hydrophobic section. Thus, the molecules accumulate at the oil/water interface and lower the IFT between the phases. Since capillary forces prevent oil from moving through water-

wet restrictions, such as pore throats, decreasing such forces can increase recovery. When the capillary number, or ratio between viscous and capillary forces, is high, viscous forces dominate and remaining oil can move. This also applies in a gravity-dominated displacement, where the Bond number, or ratio of gravity to capillary forces, needs to be high to overcome capillary trapping (James 2011).

Alkaline flooding is an enhanced oil recovery (EOR) process in which alkali is injected during a flooding process to improve the recovery of residual oil in hydrocarbon formations. As used herein, the term "alkaline flooding" includes injecting alkali in a water flood, polymer flood or a surfactant-polymer flood. The primary recovery mechanism of alkaline flooding is by improving microscopic displacement efficiency. Microscopic displacement efficiency is largely controlled by capillary forces between the reservoir fluids and the formation. In an alkaline flood, alkaline agents react with acidic components in the oil to form soap. The soap, which acts as a surfactant and is the primary driver for oil recovery, reduces the interfacial tension (IFT) between the water and oil in the reservoir allowing trapped oil globules to escape from pore-spaces in the reservoir rock. The soap also can alter the wettability of the reservoir rock, as well as, help with reducing the adsorption of other chemicals in the injection fluid by the reservoir rock.

Alkaline floods typically operate at a high pH (e.g., above a pH value of 10) to enable saponification of the acidic components in the crude oil.

High-pH Alkaline (Jennings et al., 1974; Raimondi et al., 1976) is an alternative to surfactants, if the oil contains sufficient concentration of petroleum acids of the right type, the alkali will react in-situ to form soaps, which are also surface active. The objective is the same as a surfactant flood, but since the surfactant characteristics of the soap are not

designed for the system, recovery may not be as high as with surfactants chosen specifically for the field. In some cases, alkaline flooding is assumed to induce wettability alteration of the reservoir rock, which under certain circumstances can benefit oil recovery. The disadvantage of alkaline flooding rises when injected brine contains high concentrations of divalent cations, such as calcium and magnesium, so an increase in pH can result in severe scale formation. Furthermore, conventional scale inhibitors are typically ineffective at these elevated pH conditions. Therefore, to avoid scale formation, consequent plugging, and other problems, water treatment methods such as water softening/desalination can be used.

Combinations of these chemical methods are more common. An early combination used in several fields was surfactant-polymer flooding, also called micellar-polymer flooding. A slug of surfactant is injected to mobilize the oil, followed by a polymer flood to prevent viscous fingering. Recently, a combination of all three types of injectants has shown significant promise.

Alkali-surfactant-polymer (ASP) flooding, in which operators inject a tailored mix of an alkaline compound and surfactants chosen for the specific crude oil-brine-rock system, followed by polymer slugs for mobility control. **Fig. 2** shows an ASP flood combines the best of the three chemical methods to optimize recovery.

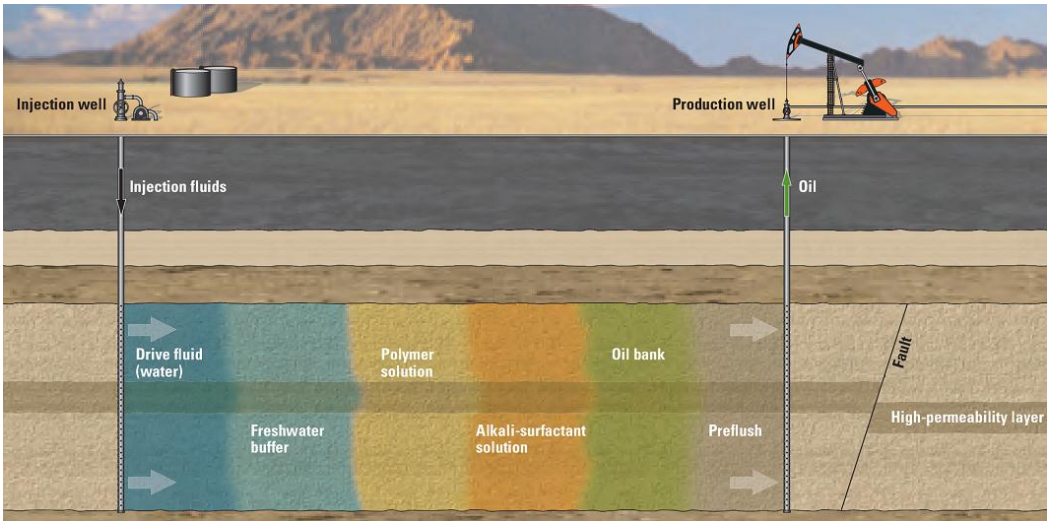


Fig. 2— Alkali-Surfactant-Polymer Flood.

The basic tool for illustrating how lower IFT reduces residual oil saturation (ROS) is the capillary distribution curve (CDC) in which the capillary number is defined as the ratio of viscosity force to capillary force as

$$N_c = \frac{v_w \mu_w}{\sigma_{wo}}$$

Where; v_w is brine velocity, μ_w is water viscosity, and σ_{ow} is oil/water interfacial tension. The CDC is a nearly horizontal plateau at small N_C until a critical value above which residual phase saturation decreases as shown in **Fig. 3**.

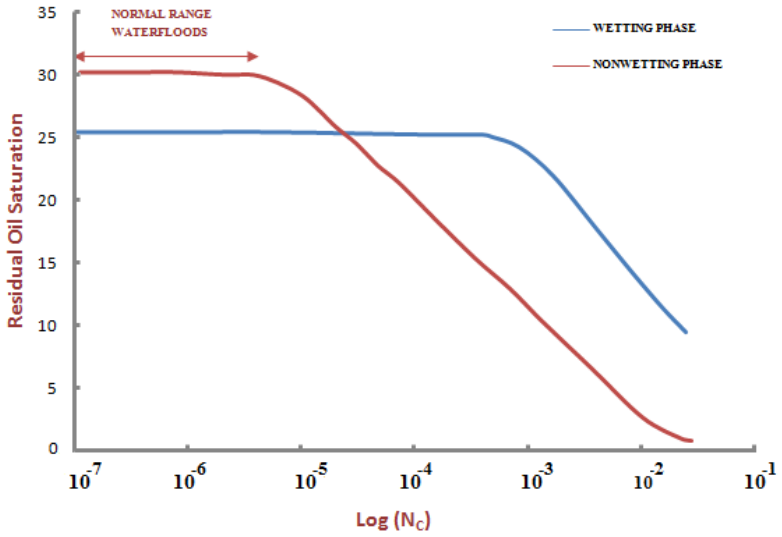


Fig. 3— Schematic of Capillary Distribution Curve

2.2 Low Salinity Brines Flooding in Carbonates

Laboratory studies conducted over a period of many years have indicated that oil recovery could be improved by injecting lower salinity water (less than about 5,000 ppm) (McGuire et al, 2005). Numerous laboratory coreflood studies have shown increased oil recovery is achieved by waterflooding using low salinity water, compared with injection of seawater or high salinity produced water (Morrow et al, 1998; Tang and Morrow, 1997; Tang and Morrow, 1999a; Tang and Morrow, 1999b).

Lowering the salinity or TDS of injected water results in lowering the oil-rock capillary pressure, reduction in oil-water interfacial tension, and finally a change in the relative permeability caused by a wettability change, usually to a mixed-wet or water-wet state.

Although a lot of research work has been done on low salinity effects in sandstones, a few of them have been reported on carbonates .It have been thought that seawater will recover more oil in carbonates than low saline water will do. This is evident in the large body of research that has been conducted over the past two decades in this area. Lager et al. (2006) concluded that unlike for sandstone with high clay content, a lower salinity waterflood does not work for carbonate reservoirs because they have minimal clay, and the mineral surface has a positive charge at typical reservoir conditions. However, a few studies recently have observed increment in oil recovery from carbonates due to low salinity water injection.

Alotaibi et al. (2010) performed extensive wettability studies on limestone cores, using formation, synthetic aquifer and seawater brines, with different concentrations. He showed that seawater or formation water made calcium carbonate substrates oil-wet but it became water wet when aquifer of deionized water was used. Additional recovery of 8.6% was also obtained in coreflood experiments when aquifer water was injected after formation brine. Investigation into the effect of injecting diluted seawater in carbonate cores have been

conducted by Yousef et al (2010). 18 to 19% incremental recovery over conventional waterflooding was obtained from coreflood experiments as a result of stepwise dilution of the seawater up to 20-times dilution. This has been attributed to the alteration of the rock wettability towards a more water wet state.

A pilot single well test was also reported by Yousef et al (2012), from which they showed that Injection of Smart Water revealed a reduction of nearly 7 saturation units in the residual oil beyond conventional seawater.

One might consider a low salinity waterflood as a precursor step before implementing a chemical EOR method. The main purpose would be to condition the reservoir by displacing as much of the resident hardness ions as possible in advance of the surfactants and polymers to be injected with the chemical slug. By itself however, some people in the industry did not consider low salinity waterflood a chemical EOR method since it does not improve mobility ratio or reduce interfacial tension.

2.3 Chelating Agents

The chelate bond dates back as far as 1893, in 1920 two scientists, G. Morton and H. Drew, coined the word “chelate”, derived from the Greek word chela, meaning “great claw” of the lobster or other crustaceans. The term chelate suggests the way in which an organic compound “clamps” onto the cationic element, which it chelates. Different terms applied to chelated minerals:

1) Chelated 2) Sequestered 3) Complexed

In order for a compound to be called a true chelating agent, it must have certain chemical characteristics. This chelating compound must consist of at least two sites capable of donating electrons (coordinate covalent bond) to the metal it chelates. For true chelation to occur the donating atom(s) must also be in a position within the chelating molecule so that a formation of a ring with the metal ion can occur.

In 1935 I.G. Farbenindustrie carried out the synthesis of EDTA (ethylenediaminetetraacetic acid) which consisted in the reaction of monochloroacetic acid with Ethylenediamine in the presence of sodium hydroxide. Another way to obtain EDTA is the reaction of Ethylenediamine with sodium cyanide and formaldehyde in the presence of sodium hydroxide. Depending on the amine used also other Aminopolycarboxylates (APCAs) can be obtained using this method. Since that time, on a worldwide scale over 100,000 tons of aminopolycarboxylic acids have been produced annually. The pulp and paper industry is a major user of EDTA.

Calcium chelating agents were first demonstrated as stimulating fluids by Fredd and Fogler (1998ab). They found that EDTA can effectively form wormhole in limestone even when injected at moderate and non-acidic pH (4-13) and at low flow rates where HCl is

ineffective. EDTA solutions don't form sludge in acid-sensitive crude oils and noncorrosive for alkaline. Fredd and Fogler (1998b) also did the kinetics studies of calcite dissolution with chelating agents using a rotating disk apparatus. The overall rate of dissolution was demonstrated to be influenced by the combined effects of the hydrogen attack, chelating reactions and the water reaction.

2.4 Chelating Chemistry

Chelating agents contain different functional groups (carboxyl, hydroxyl, ether, primary amine, tertiary amine, thiol, nitro, nitroso, and sulphine et al.) which have the ability of grabbing the metal ion and form a stable complex. Dissociated carboxyl group turns out to be the best sequestering group. Tertiary amine is the most promising group among the neutral groups (Bakken and Schöffel, 1996).

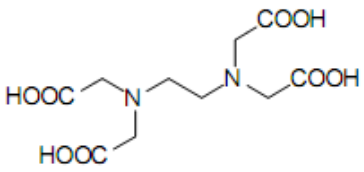
The structures of chelating agents are typically represented by H_nY where the n hydrogen's are those of the carboxylic acid groups. **Fig. 4** shows the structure of chelating agents used in petroleum industry for different applications. Aminopolycarboxylic acids undergo a stepwise loss of protons to reach their fully ionized state, as shown by Eqn. 1 through **Eqn. 4** for EDTA or CDTA (Mahmoud et al, 2012).

$$H_4Y \rightleftharpoons H_3Y^{-1} + H^+ \quad (1)$$

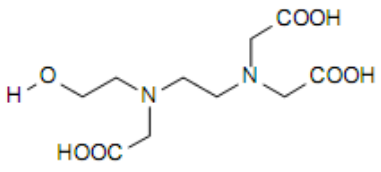
$$H_3Y^{-1} \rightleftharpoons H_2Y^{-2} + H^+ \quad (2)$$

$$H_2Y^{-2} \rightleftharpoons HY^{-3} + H^+ \quad (3)$$

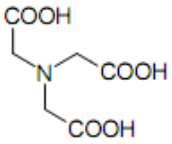
$$HY^{-3} \rightleftharpoons Y^{-4} + H^+ \quad (4)$$



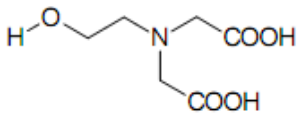
Ethylenediaminetetraacetic acid (EDTA)



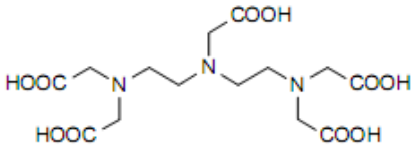
Hydroxyethylethylenediaminetriacetic acid (HEDTA)



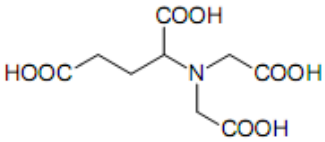
Nitrilotriacetic acid (NTA)



Ethanoldiglycinic acid (EDG) or
Hydroxyethyliminodiacetic acid (HEIDA)



Diethylenetriaminepentaacetic acid (DTPA)



L-Glutamic acid, N, N-diacetic acid (GLDA)

Fig. 4— Structure of chelating agents used in petroleum industry (Mahmoud et al, 2010)

The distribution of ionic species depends on the equilibrium constants for each of the dissociation reactions and on the solution pH. The basic idea behind these chelating agents is the sequestration of metal ions and preventing any metal precipitation in carbonate

formations. The conjugate bases of the chelating agents have the ability to chelate different ions such as iron and calcite which present in reaction solutions. The affinity of conjugate base (ligand), A^{n-}, for different ions, M^{m+}, is dependent on stability of the formed conjugate base and ion complex molecule, the chelation ability, affinity, is defined by the formation

constant KF which is the ratio of the chelated metal ion in equilibrium with the free metal ion and chelating agent in solution as expressed in **Eqn. 5**, and **6** (Al-Harbi, 2011).

$$A^{n-} + M^{m+} \rightleftharpoons MA^{m-n} \quad (5)$$

$$K_F = \frac{[MA^{m-n}]}{[A^{n-}][M^{m+}]} \quad (6)$$

The higher the formation constant, the stronger is the ion-conjugate base complex. **Table 1** lists the chelating agents complexes with different minerals (Freiner 2001). Chelated mineral complexes with log K_F greater than 8 are stable chelates and from Table 1 we can see that EDTA and ETPA form stable chelates with calcium and magnesium while HEDTA chelates with Calcium is more stable than its chelate with magnesium.

Table 1- Equilibrium constants for various metal/ligand chelates (Freiner 2001)

Ligand	MW		Log of stability constant (K_F) 1:1 complex						
	Acid	Na Salt	Al(III)	Fe(II)	Fe(III)	Cu(II)	Mg(II)	Ba(II)	Ca(II)
Formic acid	46	N/A	1.4	N/L	3.1	1.4	1.4	1.4	1.4
Acetic acid	60	N/A	1.5	1.4	3.4	1.8	1.3	1.1	1.2
Citric acid	192	256	11.7	4.4	11.5	5.9	3.4	2.8	3.5
NTA	191	257	11.4	8.3	15.9	12.9	5.5	4.8	6.4
HEDTA	278	344	14.4	12.2	19.8	17.4	7.0	6.2	8.4
EDTA	292	380	16.5	14.2	25.0	18.8	8.8	7.8	10.7
DTPA	393	503	18.7	16.5	28.0	21.1	9.3	8.9	10.9
HEIDA	177	221	7.7	6.8	11.6	11.7	3.5	3.4	4.8

The stability of the calcium chelate influences the ability of the chelating agent to dissolve calcite. Strong calcium chelating agents such as CDTA, DTPA, and EDTA exhibit a relatively high rate of dissolution in the pH range of 8.4 to 12 (Fredd 1998b). In contrast, weak calcium complexing agents, such as acetate, have no significant effect on

the rate of dissolution over the same pH range In addition, nitrilotriacetic acid (NTA), which forms a relatively weak chelate with calcium (Log K_F of 6.4 (Martell and Calvin, 1956), was found to be ineffective for calcium carbonate stimulation (Fredd, 1998).

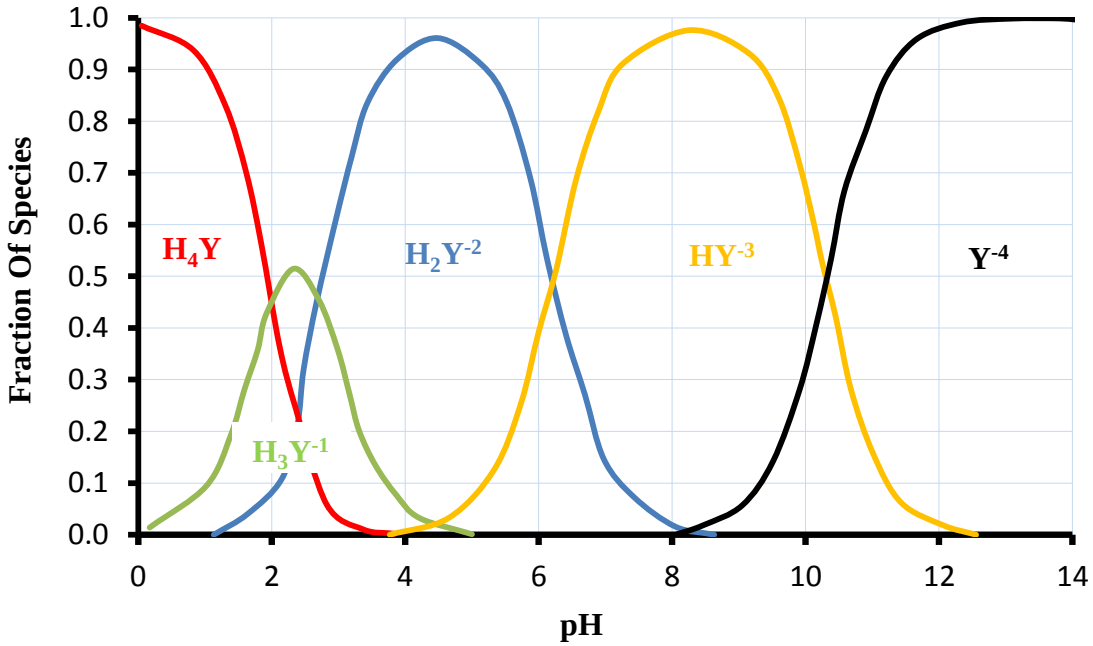


Fig. 5— Distribution of ionic species of EDTA at room temperature (Freiner 2001).

The distribution of ionic species for EDTA at room temperature is shown in **Fig. 5**. At a pH of approximately 4.5, EDTA is in the form of H_2Y^{2-}. At higher pH values of about 8.5 and 13 EDTA successively deprotonates to the HY^{-3} and Y^{-4} species respectively .Chelating agents such as EDTA and HEDTA have been used as standalone stimulation fluids and as an alternative to HCl. Chelating agents stimulates by means of complexing the metal components of the carbonate matrix; EDTA was first used for removal of calcium carbonate scale from sandstone reservoir at the Prudhoe field (Tyler et al 1985). Since that day few people have tested the chelating agents as a stimulation fluid in carbonate

reservoirs starting from Fred and Fogler (1998), Huang et al (2003), Frendier et al (2003-2004), and Mahmoud et al (2012). In neutral environments three reactions have been shown to occur simultaneously for dissolution of carbonate rock surface.

$$CaCO_3 \rightleftharpoons Ca^{2+} + HCO_3^- \quad (7)$$

$$H_2CO_3 + CaCO_3 \rightleftharpoons Ca^{2+} + 2HCO_3^- \quad (8)$$

$$H_2O + CaCO_3 \rightleftharpoons Ca^{2+} + HCO_3^- + OH^- \quad (9)$$

When chelating agents are present, the free calcium ions in solution are sequestered and reactions **7** through **9** are driven in the forward direction depending on the pH which define the species (Distribution of ionic species) of the chelating agent, In case of using HEDTA for example Table 2 shows the different reaction at different pH condition for example at pH 13, the fully dissociated form of EDTA exists. A number of chemical reactions occur at the solid-liquid interface. The key dissolution reaction at high pH is due to ligand attack, which is expressed by Eqn.10.

$$L^{-4} + CaCO_3 \rightleftharpoons CaL^{-2} + CO_3^{-2} \quad (10)$$

Table 2- Distribution of ionic species at different PH condition and its reaction with calcite (Freiner 2001).

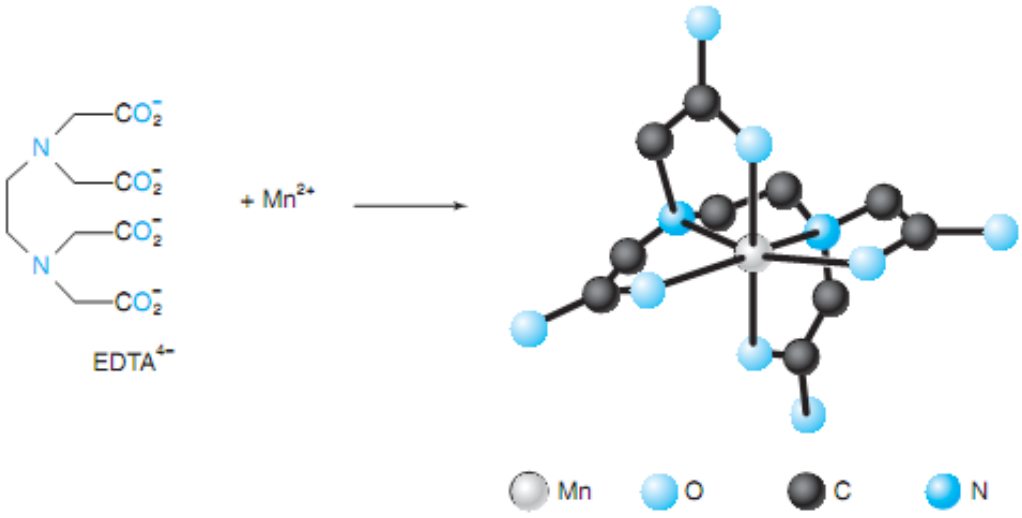
pH	HEDTA Species	Reaction with Calcite
4-5	H_2Y^{-2}	$H_2Y^{-2} + CaCO_3 \leftrightarrows CaY^{-2} + H_2CO_3$
8.5	HY^{-3}	$HY^{-3} + CaCO_3 \leftrightarrows CaY^{-2} + HCO_3^-$
13	NaY^{-3}	$NaY^{-3} + CaCO_3 \leftrightarrows CaY^{-2} + NaCO_3$

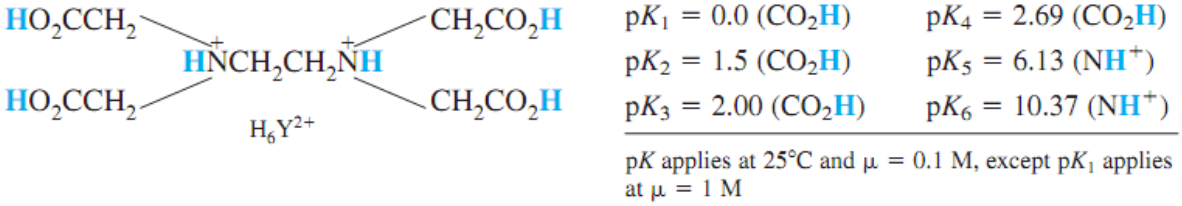
2.5 EDTA

EDTA is a merciful abbreviation for ethylenediaminetetraacetic acid, a compound that forms strong 1:1 complexes with most metal ions (**Fig. 6**) and finds wide use in quantitative analysis. Chaberck mentioned that EDAT is capable of combining stoichiometrically with virtually every metal in the periodic table (Chaberck & Martell, 1959). With divalent or trivalent metal ions, a neutral or anionic metal chelate results. The metal is largely prevented from reacting with competing anions, and its solubility is greatly increased. The effectiveness of EDTA as a chelate for a particular metal ion is given by its stability constant with the metal ion.

Chelation potential is affected by pH, the molar ratio of chelate to metal ion, and the presence of competing metal ions capable of forming complexes with EDTA (Plumb et al., 1950; Martell, 1960; Hart, 1984). The stability constants for different metal–EDTA complexes vary considerably, and any metal that is capable of forming a strong complex with EDTA will at least partially displace another metal. EDTA plays a larger role as a strong metal-binding agent in industrial processes and in products such as detergents, cleaning agents, and food additives that prevent metal-catalysed oxidation of food. EDTA is an emerging player in environmental chemistry.

EDTA is the most widely used chelating agent, although not the only useful aminocarboxylic acid chelating agent. As it is hexadentate, it is also a hexaprotic acid or base. In **Fig. 6**, you can clearly see that there are 4 acidic protons as it is a tetra-carboxylic acid. But the two amino groups would also be protonated at low pH values, so these are the 5^{th} and 6^{th} acidic protons.





pK_1 = 0.0 (CO_2H)	pK_4 = 2.69 (CO_2H)
pK_2 = 1.5 (CO_2H)	pK_5 = 6.13 (NH^+)
pK_3 = 2.00 (CO_2H)	pK_6 = 10.37 (NH^+)

pK applies at 25°C and μ = 0.1 M, except pK_1 applies at μ = 1 M

Fig. 6— Metal complexing by EDTA.

The first four p*K* values apply to carboxyl protons, and the last two are for the ammonium protons. The neutral acid is tetraprotic, with the formula H_4Y which can be dried at 140°C for 2 h and used as a primary standard. It can be dissolved by adding NaOH solution from a plastic container. NaOH solution from a glass bottle should not be used because it contains alkaline earth metals leached from the glass. Reagent-grade $Na_2H_2Y.2H_2O$ contains ~ 0.3% excess water. It may be used in this form with suitable correction for the mass of excess water or dried to the composition $Na_2H_2Y.2H_2O$ at 80°C. The certified reference material $CaCO_3$ can be used to standardize EDTA or to verify the composition of standard EDTA.

The equilibrium constant for the reaction of a metal with a ligand is called the formation constant, K_f, or the stability constant:

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4} \qquad K_f = \frac{[MA^{n-4}]}{[Y^{4-}][M^{n+}]} \qquad \text{Equation } 11-5$$

Table 3- Formation constants for metal-EDTA complexes (Martell et al, 2001).

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.95	V^{3+}	25.9[a]	Tl^{3+}	35.3
Na^+	1.86	Cr^{3+}	23.4[a]	Bi^{3+}	27.8[a]
K^+	0.8	Mn^{3+}	25.2	Ce^{3+}	15.93
Be^{2+}	9.7	Fe^{3+}	25.1	Pr^{3+}	16.30
Mg^{2+}	8.79	Co^{3+}	41.4	Nd^{3+}	16.51
Ca^{2+}	10.65	Zr^{4+}	29.3	Pm^{3+}	16.9
Sr^{2+}	8.72	Hf^{4+}	29.5	Sm^{3+}	17.06
Ba^{2+}	7.88	VO^{2+}	18.7	Eu^{3+}	17.25
Ra^{2+}	7.4	VO_2^+	15.5	Gd^{3+}	17.35
Sc^{3+}	23.1[a]	Ag^+	7.20	Tb^{3+}	17.87
Y^{3+}	18.08	Tl^+	6.41	Dy^{3+}	18.30
La^{3+}	15.36	Pd^{2+}	25.6[a]	Ho^{3+}	18.56
V^{2+}	12.7[a]	Zn^{2+}	16.5	Er^{3+}	18.89
Cr^{2+}	13.6[a]	Cd^{2+}	16.5	Tm^{3+}	19.32
Mn^{2+}	13.89	Hg^{2+}	21.5	Yb^{3+}	19.49
Fe^{2+}	14.30	Sn^{2+}	18.3[b]	Lu^{3+}	19.74
Co^{2+}	16.45	Pb^{2+}	18.0	Th^{4+}	23.2
Ni^{2+}	18.4	Al^{3+}	16.4	U^{4+}	25.7
Cu^{2+}	18.78	Ga^{3+}	21.7		
Ti^{3+}	21.3	In^{3+}	24.9		

The stability constant is the equilibrium constant for the reaction $M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$. Values in table apply at 25°C and ionic strength 0.1 M unless otherwise indicated. a. 20°C, ionic strength = 0.1 M. b. 20°C, ionic strength = 1 M.

Note that K_f for EDTA is defined in terms of the species Y^{4-} reacting with the metal ion. The equilibrium constant could have been defined for any of the other six forms of EDTA in the solution. Equation 11-5 should not be interpreted to mean that only Y^{4-} reacts with metal ions. **Table 3** shows that formation constants for most EDTA complexes are large and tend to be larger for more positively charged cations.

2.6 Degradation of EDTA

Degradation of EDTA in natural conditions proceeds due to growth of specific bacteria from the subclass of Procteobacteria. Several bacteria strains such as the gramnegative strain BNC1 were also found to be able to degrade EDTA. It was found that M(II)-EDTA complexes with the stability constants below 10^{12} such as Ba(II), Mg(II), Ca(II) and Mn(II) were degraded whereas chelates with higher stability constants such as Fe(III), Co(II), Cd(II), Pb(II), Ni(II) or Cu(II) (**Table 4**) were not metabolized (Nörtemann, 2005).

The system of EDTA transport is based on its extracellular evolution with metal ions found in the solution and intracellular absorption and precipitation of metals combined with EDTA to form complexes (Witschel, 1999). It should be noticed that probably only the complexes of stability constants $<10^{14}$ can be transported inside the cell. Contrary to EDTA, transport of NTA inside the bacterium cell has not been well recognized yet. It is assumed that it gets inside the cell through the active transport. As established the metabolic intermediates of EDTA biodegradation include ethylenediaminetriacetic acid (ED3A), N′N′-ethylenediaminediacetic acid (N′N′-EDDA), ethylenediaminemonoacetic acid (EDMA), ethylenediamine (ED) and glyoxylate. The metabolic intermediates of NTA biodegradation are iminodiacetic acid (IDA), glycine, and glyoxylate (Yuan & VanBriesen, 2008). EDTA and DTPA are also reported to be photodegradable in the form of Fe(III) complexes (Cokesa, et al. 2004a). The process is pH dependent. It was found that it is faster in acidic conditions.

Table 4- Comparison of the stability constants of M(II)-L=1:1 complexes with EDTA, NTA, DTPA and NTMP (Martell & Smith, 1982). (— Data not available)

M(II)	EDTA	NTA	DTPA	NTMP
Al(III)	16.5	11.4	18.6	—
Ba(II)	7.9	4.8	8.7	—
Ca(II)	10.7	6.4	10.8	5.75
Cd(II)	16.5	9.8	—	6.4
Co(II)	16.5	10.4	18.8	7.5
Cu(II)	18.8	12.9	21.2	10.7
Fe(II)	14.3	8.3	16.2	—
Fe(III)	25.1	15.9	28	—
Hg(II)	21.5	—	26.4	—
Mg(II)	8.8	5.5	9.3	4.3
Mn(II)	13.9	7.5	15.2	—
Ni(II)	18.4	11.5	20.1	7.1
Pb(II)	18	11.4	18.8	—
Zn(II)	16.5	10.6	18.2	8.2

2.7 In-situ CO_2 Generation

Enhanced oil recovery using CO_2 flooding required a mobility control agents otherwise CO_2 will migrate to the upper part of the reservoir especially for thick reservoirs and the lower part of the reservoir will remain unsweept from oil. CO_2 injection into hydrocarbon reservoir is reported by many researchers to be one of the best enhanced oil recoveries. CO_2 for enhanced oil recovery has favourable characteristics such as miscibility between CO_2 and oil under most reservoir conditions, intermediate component extraction and heavy oil viscosity reduction which is named CO_2 flooding process. However, CO_2 flooding processes frequently experience viscous fingering and gravity override problems because of the very low CO_2 density and viscosity when compared to the crude oil. As a result, sweep efficiency decreases and significant amounts of oil are left behind (Chang and Grigg 1999; Apaydin and Kovscek 2001; Panahi 2004; Le et al. 2008).

The need for mobility control during CO_2 flooding motivated a lot of investigators to look for foam processes, which involves the injection of CO_2 together with an aqueous solution of a CO_2-foaming agent (Chang and Grigg 1999). CO_2 has a very low viscosity in comparison to oil and water. However, when CO_2 is a dispersed phase, as in foam, its apparent viscosity is greatly increased and its mobility will be improved (Liu et al. 2006). From the time when the use of foam in reservoirs was first proposed in a patent by Bond and Holbrook which is reported by (Bernard and Holm. 1964), it was usually implicitly assumed without specific mention, that foam would preferentially impede flow in the higher permeability layers or fractures in the reservoir that had already been swept of their oil. It was assumed without evidence that the unswept parts of the reservoir would remain at least as accessible and available to have their content displaced and forced into the production wells. The foaming process success depends on foam concentration,

compatibility with the reservoir rock, stability in solution for long time, and thermal stability. Surfactants have been used as foaming agents but the main problem with surfactants is the thermal stability, they cannot stand for temperatures more than 100^{o}C.

3.7.1 Previous Methods to Generate CO_2 In-Situ

Shia et al. (2010) developed a method to generate CO_2 in-situ. The purpose of this study is to investigate compounds that can generate carbon dioxide *in-situ* . They used ammonium carbamate to produce a significant amount of carbon dioxide when the temperature is elevated to 85° C. In contrast, negligible CO_2 is detected while heating up the methyl carbamate to a similar temperature range. Ammonium carbamate is further studied in a one-dimensional sand pack column. Ammonium carbamate results in the production of CO_2 in column studies at 80^{o}C and 90^{o}C and also results in a decrease in oil viscosity. The additional injection of a 0.5 PV of 3% ammonium carbamate solution with a polymer + surfactant chemical flood improved crude oil recovery by 9.7% OOIP compared to a polymer + surfactant chemical flood without carbamate. However, there is negligible oil recovery without the presence of surfactant for studies using light oils, decane and Arrow crude oil. They used this method in sand pack column they did not try it with actual cores. The recovery from this method was very low compared to the recovery of the new method that we are introducing. The maximum recovery they got in their experiment was 43% from the residual oil recovery after surfactant/polymer injection; in our method we recovered more than 80% from the residual oil after seawater injection. Our method is very simple and there is not complex additives are required.

Gumersky et al. (2000) introduced a new method to generate CO_2 in-situ, this method includes the injection of sodium carbonate with hydrochloric acid (HCl) into the formation

and wait for 24 hours for the reaction to occur then the CO_2 will be generated. The problem with this method is that HCl is very corrosive; therefore, corrosion inhibitors should be added (high cost). The corrosion inhibitor may reverse the wettability of the formation and make it oil wet, in turn water wetting agents should be added. A lot of additives should be used in this method, also it cannot be used in carbonate reservoirs because HCl will react with carbonate immediately when injected and the sodium carbonate will remain in the reservoir without reaction and it will cause damage. This method is very expensive and uncontrolled.

CHAPTER 3

MOTIVATION OF THE WORK

3.1 Clear Understanding of Low-Salinity Effect

The idea of injecting low salinity water into petroleum reservoir has been addressed since the 1960s (Yousef et al., 2012) later many laboratories and organizations have grappled with the opportunities and problems associated with identifying, reproducing, and explaining the low-salinity effect (LSE).

Wettability alteration towards more water-wet was reported to be the mechanism for the additional oil recovery even though several mechanisms for the wettability alteration have been proposed in the literature; however, there is no consensus about the primary mechanism. The proposed mechanisms can be summarized as follows:

1- Fines migration (Tang and morrow 1999).
2- pH increase leading to IFT reduction (McGuire et al. 2005).
3- Multi-ion exchange (large et al. 2006; Berg et al. 2009).
4- Double layer expansion (Ligthelm et al. 2009; Doust et al. 2009; Berg et al. 2009).
5- Rock Dissolution (Zaid el al. 2012; Hiorth et al. 2010)

The most important mechanisms of these proposed wettability alteration mechanisms which lead to additional recovery will be discussed in the next section.

3.1.1 Fine Migration or Permeability Reduction

This mechanism was proposed for the increase in oil recovery from sandstone cores when flooded with LowSal brines, it was explained in the way that low salinity solutions affect the dispersion of clay and silt in the formation (release of clay particles). The clay and silt, upon dispersion, become mobile and follow the paths taken by the greatest proportion of the flowing water (Tang and Morrow, 1999).

These paths are the domains of high permeability, and the mobile clay and silt become lodged in the smaller pore spaces of these domains and reduce the flow of water through these pore spaces. The permeability of the domains where clay and silt lodge is accordingly reduced, and the water is forced to take other flow paths. As a result, the permeabilities in these domains within the formation become more uniform. Reduction in permeability in the more permeable domains improves the mobility ratio of waterflood. Premature breakthrough is thus reduced, and the efficiency of the waterflood is improved (Boston et al., 1969).

3.1.2 Multicomponent Ion Exchange

Due to the different affinities of ions on rock surfaces, the result of multicomponent ion exchange (MIE) is to have multivalents or divalents such as Ca^{2+} and Mg^{2+} strongly adsorbed on rock surfaces until the rock is fully saturated.

Multivalent cations at clay surfaces are bonded to polar compounds present in the oil phase (resin and asphaltene) forming organo-metallic complexes and promoting oil-wetness on rock surfaces. Meanwhile, some organic polar compounds are adsorbed directly to the mineral surface, displacing the most labile cations present at the clay surface and enhancing the oil-wetness of the clay surface.

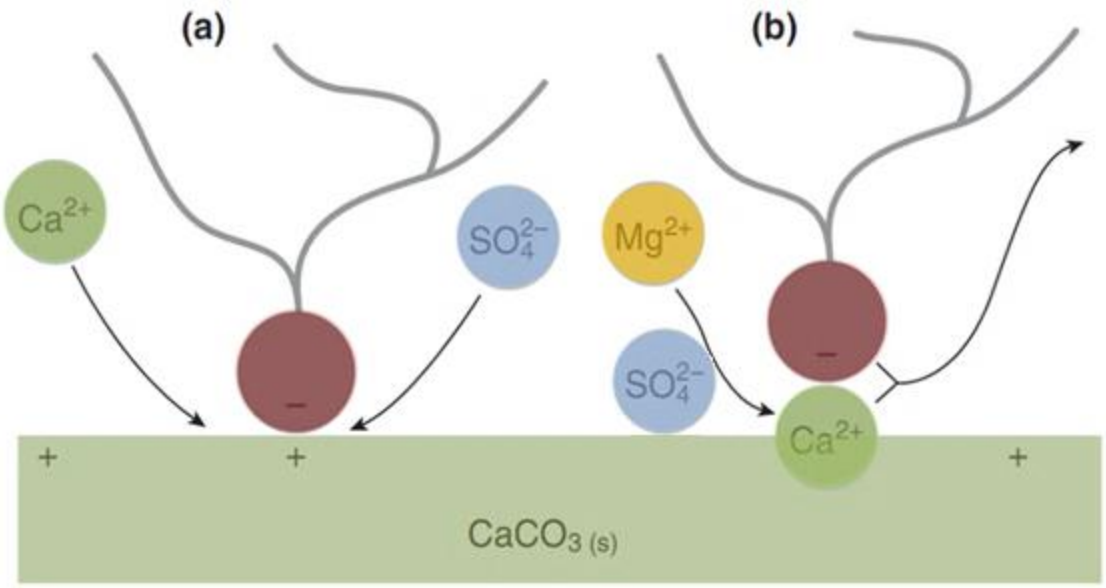


Fig.7 — Schematic model of the suggested mechanism for the wettability alteration induced by seawater, (Zhang et al. 2007).

The cation exchange capacity will be higher in carbonate reservoirs compared to sandstone because carbonate contains lot calcium in the matrix. Ca^{2+}, $Mg^{2+,}$ and SO_4^{2-} were the active ions in the wettability alteration process (Austad et al, 2009).

At low and high temperatures, SO_4^{2-} adsorbs onto the positively charged chalk surface. Ca^{2+} may react with the adsorbed carboxylic group (as a result of reduced rock surface positive charge caused by SO_4^{2-} adsorption) to form a complex and release it from the surface (as shown in part a of the **Fig. 7)**. At high temperature, Mg^{2+} may displace the Ca^{2+}–carboxylate complex (as shown in part b of **Fig. 7**).

This suggests that the small and strongly solvated Mg^{2+} is able to substitute Ca^{2+} in a Ca^{2+}–carboxylate complex, although the Ca^{2+}–carboxylate bond is normally stronger than the Mg^{2+}–carboxylate bond. As SO_4^{2-} adsorbs on the chalk surface, more divalents can be

adsorbed on the surface due to less electrostatic repulsion (Zhang et al., 2007a). As the complexes are displaced from the chalk surfaces, the surfaces become more water-wet.

During the injection of LSW, MIE will take place, removing organic polar compounds and organo-metallic complexes from the surface and replacing them with uncomplexed cations (Lager et al., 2006).

In theory, desorption of polar compounds from the clay surface should lead to a more water-wet surface, resulting in an increase in oil recovery.

3.1.3 Rock Dissolution

Two studies have indicated to rock dissolution as the dominant mechanism of wettability alteration and hence increased recovery *(Hiorth et al., 2010; Zahid et al., 2012).* Hiorth et al. (2010) investigated water chemistry effect on the surface charge and rock dissolution on a pure calcium carbonate rock. He concluded from his chemical model that changes in solution chemistry do not change the surface potential of carbonate in a fashion that can explain how these changes increase oil recovery in spontaneously imbibition experiments. A good candidate was thought to be carbonate dissolution as shown by the chemical model, dissolution of calcite took place in the temperature range where enhanced imbibition was observed. **Fig. 8** shows the dissolution mechanism proposed by Hiorth et al. At low temperature, seawater is in equilibrium with calcite, but at higher temperature calcium in the seawater reacts with sulfate and anhydrite is precipitated. When anhydrite is formed the aqueous phase loses calcium, and calcium has to be supplied from the rock for the solution to remain in equilibrium with calcite. The source of Ca^{2+} ions must be calcite dissolution. If the calcite dissolution takes place where the oil is adsorbed, then the oil can be liberated from the rock.

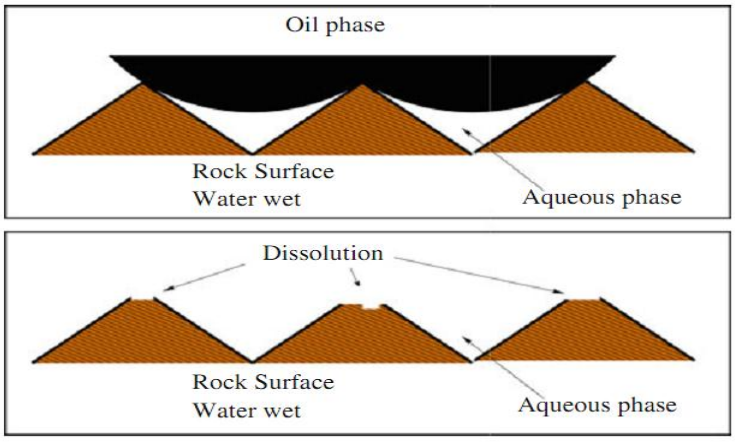


Fig. 8—Top: A section of the pore space, before any dissolution reaction. The surface is rough and oil is attached where there is a large curvature and the water film is broken. Bottom: Dissolution of the chalk surface has taken place where the oil was attached *(Hiorth et al., 2010).*

Recently Austad et al. (2011) concluded that tertiary low-salinity EOR effects can be obtained in carbonates provided that anhydrite is present in the matrix and the catalytic agent sulfate is created in the matrix because of dissolution of anhydrite. Zahid et al (2012) experimentally investigated the oil recovery potential of low salinity waterflooding for carbonate rocks free of anhydrite, they reported an additional oil recovery by sequential injection of various diluted seawater. Finally they concluded that dissolution of rock material is a possible mechanism for the incremental oil recovery with low salinity brines from the carbonate reservoir core plugs at 90^{o}C.

This proposed work will be able to confirm that the recovery mechanism is dissolution of rock material specially Ca^{2+} and the role of sulfate ions is only enhancing the rock to give more Ca^{2+} to balance the decreased Ca^{2+} caused by calcium sulfate precipitation in limestone cores. The dissolution of the rock material enhanced the oil recovery by changing the rock surface wettability towards more water wet conditions which will help to unlock the trapped oil in rock pore space.

In our work the chelated Ca^{2+} by Na_4EDTA solution will cause a decrease in the Ca^{2+} concentration in the injected solution which will enhance the rock to release more calcium cations from its surface to reach equilibrium with the injected solution. Na_4EDTA will continue to chelate Ca^{2+} and hence preventing the formation of Calcium sulfate precipitant ($CaSO_4$ (s)).

3.2 Formation Damage due to Low Salinity EOR in Carbonate Reservoirs

Calcium sulfate precipitant ($CaSO_4$ (s)) which was the common problem causing permeability reduction in low salinity waterflooding and even in seawater flooding as show by the increased pressure drop in **Fig. 9(b),** (Zahid et al., 2012).

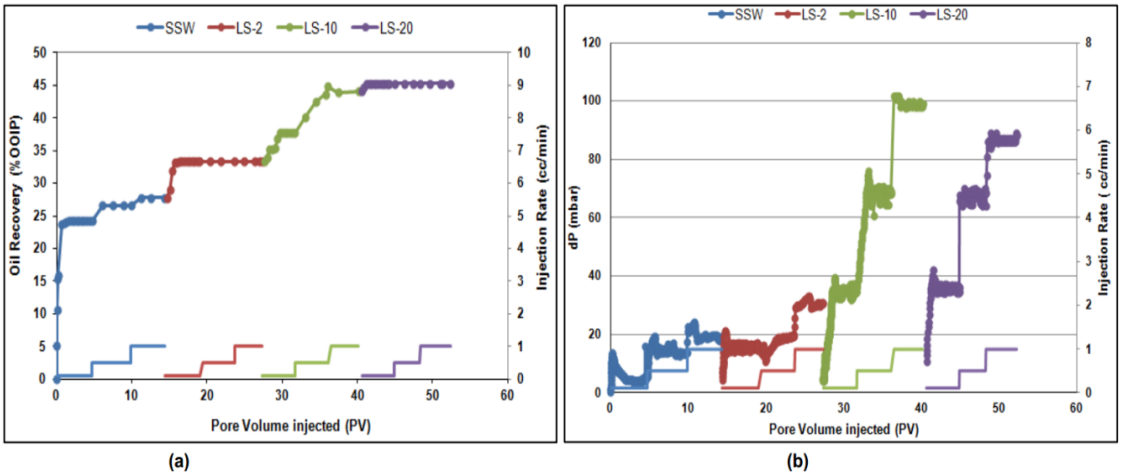


Fig. 9— (a) Oil recovery as a function of pore volume injected for a carbonate core, (b) pressure drop variation as a function of pore volume injected (Zahid, 2012).

For a petroleum engineer the pressure drop means losing the infectivity, for example the pressure drop in **Fig. 9 (a)** will make the injectivity 7 times down by injection of LS-10 brine. The newly proposed flooding method will avoid all of these problems by preventing scale precipitation in the reservoir.

The improved oil recovery observed by decreasing the NaCl concentration in seawater is related to a decrease in the nonactive ions in the ionic double layer at the carbonate surface, which allows for better access of the active ions (Ca^{2+}, Mg^{2+}, and SO_4^{2-}) to the surface. Both the imbibing rate and the ultimate oil recovery from displacement tests increased.

Fig. 11 shows the pressure drop profile versus injection rate during low and high salinity seawater injection through oil-saturated limestone cores. Diluting the seawater ten times increased the pressure drop 10 times at 0.1 cc/min injection rate and five times at 0.5 and 1 cc/min injection rates. Diluting seawater should decrease its viscosity because its density goes down with dilution. The flooding procedures were the same in all experiments that were performed for high salinity seawater. Increasing the pressure drop during low salinity diluted seawater flooding instead of seawater can be attributed to the calcium Sulfate precipitation.

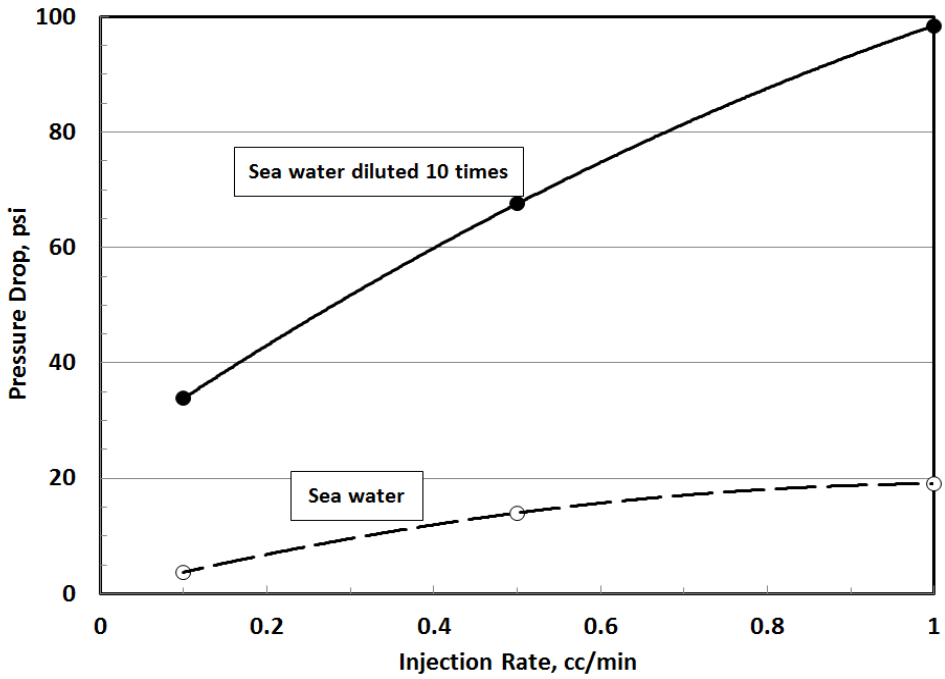


Fig. 10— Pressure drop as a function of injection rate for high salinity (seawater) and low salinity (seawater diluted 10 times) in limestone core at 90oC. (After Zahid et al. 2012).

As shown in **Fig. 10** the pressure drop increase ratio was less at higher injection rate due to the low contact time between the injected water and brine, therefore, the precipitation rate of calcium sulfate will be lower at injection rates 0.5 and 1 cc/min compared to that at 0.1 cc/min.

Kumart et al. (2007) showed that the solubility of $CaSO4.2H_2O$ increases with an increase in the concentration of NaCl in solution, and decreases with an increase in the concentration of CaCl2. **Fig. 11** shows the relation between the concentration of NaCl in brine and calcium sulfate solubility in the water. Diluting the seawater means reducing NaCl concentration in the injected water as shown in Fig. 10 which means reducing the ability of the injected brine to dissolve calcium sulfate and this is another problem leading to permeability reduction also. Diluting seawater ten times will decrease the calcium sulfate solubility in the water dramatically and the precipitation rate of calcium sulfate will increase and the pressure drop will increase.

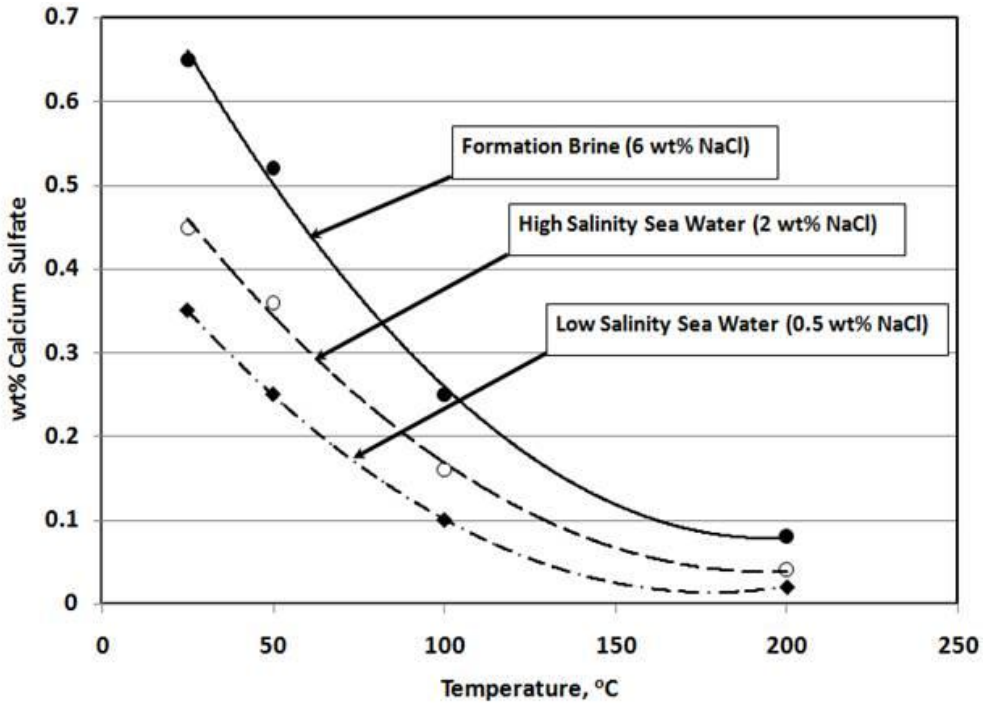


Fig. 11— Effect brine NaCl concentration on the dissolved calcium sulfate as a function in temperature (*Carlberg, Matthews., 1973).*

Sheikholeslami et al. (2012) investigated the interactive effect of CaSO4 precipitation in the range of 0.06 M to 0.10 M, in NaCl solution ranging from 0.5 M to 1.5 M, They

examined the reduction of both Ca^{2+} and SO_4^{2-} ionic species in a non-precipitating NaCl solution (**Figs**. **12a** and **12b**). They concluded that kinetics of CaSO4 was strongly affected by the salinity levels, as concentration of NaCl increased less anhydrite can be precipitated out of the solution. From these figures we can conclude that low salinity water injection was good in oil recovery but it caused calcium sulfate precipitation through the core and this will reduce the water injectivity with time and the formation damage will occur in the reservoir.

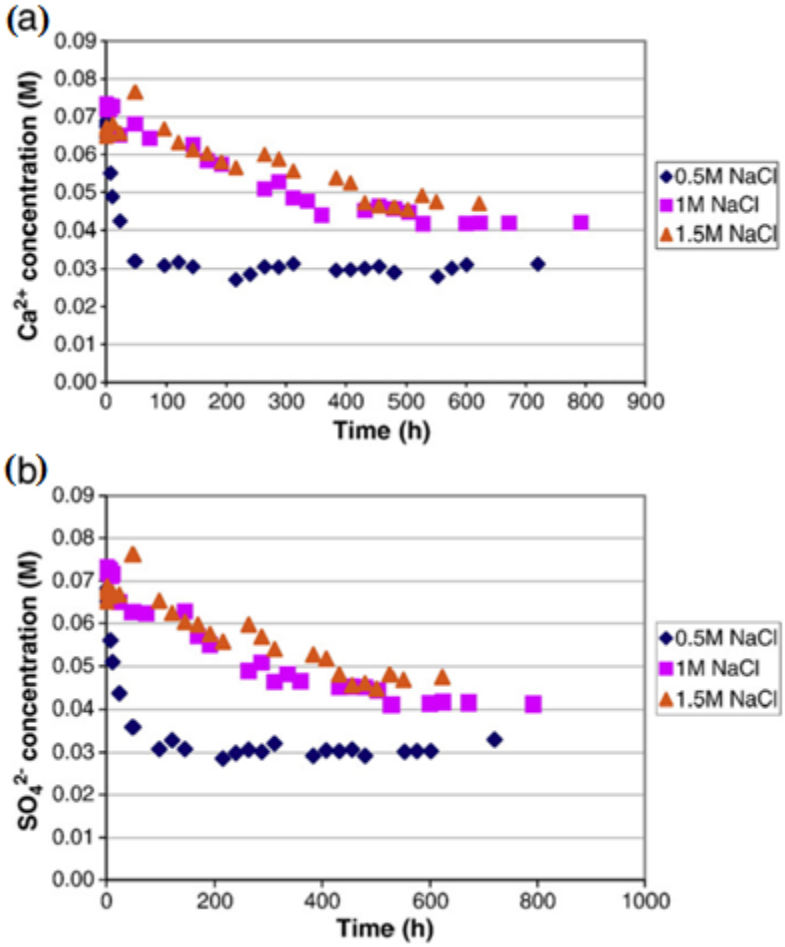


Fig. 12—(a) Precipitation of $CaSO_4$ in presence of NaCl as monitored by reduction of Ca^{2+} concentration. (**b)** Precipitation of CaSO4 in presence of NaCl as monitored by reduction of SO_4^{2-} concentration (Sheikholeslami et al. ;2012).

3.3 Significance of the Research

This work validate the thought of using chelating agents as a new chemical flooding fluid to improve oil recovery from carbonate reservoirs. This new method will overcome a lot of problems and complexity encountered during other chemical EOR methods and the study represents the first step towards implementation of the new method on industrial scale. The new EOR fluid system in carbonate reservoirs can be claimed by the following:

- Adding EDTA to the injected seawater will increase the pH of the solution up to a value of 13; in several studies it was proved that high pH solutions reduced the surface tension, interfacial tension, and contact angle between the oil and the rock. In turn, the oil recovery will increase (Al-Rossies et al 2010 and McGuire et al. 2005).
- EDAT contains four carboxylic groups that by nature have low IFT.
- During the water injection process, the rust of the well tubular will be injected into the formation; this will cause the precipitation of asphaltene and sludge which will lower the well injectivity. Having EDTA in the injected water will chelate all the iron and prevent the formation of asphaltene, therefore, EDTA acted as anti-sludge agent.
- Seawater or low salinity water contains sulfate. This water if injected into a high calcium concentration containing formation brine (which is the case in Arabian Gulf for example you have about 19,000 ppm Ca) will precipitate calcium sulfate and cause formation damage and will reduce the well injectivity with time. EDAT will chelate all calcium in solution and will not allow the precipitation of sulfate scale. Diluting seawater will decrease the sodium chloride content and this will lower the solubility of calcium sulfate. It was found that smart water increases the oil recovery but the pressure drop increases due to sulfate precipitation, which means reducing the injectivity.

- If seawater or low salinity water were used for water injection and there was a scale of calcium sulfate, the new system can be used for recovery and the EDTA in the solution will dissolve the calcium sulfate, in turn the formation injectivity will increase.
- EDAT solutions viscosity goes up when chelate more cations (calcium, iron, magnesium, etc), this will act somehow as polymer and the mobility of the injected water will decrease allowing for more oil recovery as show in **Table 5**.

Table 5- viscosity and density of 5 wt% EDTA solution prepared in de-ionized water at 70^{o}F

Calcium Concentration, ppm	**Viscosity, cP**	**Density, g/cc**
0	1.45	1.101
5000	1.64	1.115
10000	1.98	1.134
20000	2.14	1.187
30000	2.67	1.221

- EDTA solution when injected into the formation it will chelate all cations from solutions, this will allow the cations exchange between the rock surface and the injected solution (actually this is the dissolution mechanism of high pH chelating agent) and this will change the wettability of carbonate rock towards more water wet.

CHAPTER 4

Methodology and Experimental work

The first aspect of this research is to test the ability of Na_4EDTA to enhance oil recovery from limestone reservoir rock. The tasks for the research will be conducted systematically so that the objectives of the proposed research will be achieved upon completion of these tasks. The tasks are outlined below;

Task 1: Comparing EDTA chelating agent solution with seawater flooding

1. Characterization of the core samples, oil, brine, and chelating agents.
2. Saturating the core with prepared reservoir brine.
3. Flooding the core with crude oil with defined density and viscosity to establish initial water saturation for the cores to be used for EOR testing.
4. Aging at 90°C in crude oil for 2 weeks.
5. Displacing the crude oil with seawater till residual oil saturation followed by chelating solution.
6. Repeating step (4) for another core plug with chelating agent solution instead of seawater.

Task 2: Testing Chelating Agents for In-situ CO_2 Generated EOR.

1. The OOIP will be recovered using low pH chelating agents/seawater solution.
2. The in-situ generated CO_2 and High pH chelating agent will be employed to recover more oil using alternate mode injection different chelating agents/seawater solutions.

3. A seawater compatible low pH chelating agent (BCA) will be used for CO_2 generation.

Task 3: Testing the Effect of High pH Chelating Agents on the Brine Saturated Limestone during Seawater Injection.

Through this task I will prove through core flooding tests that High pH chelating agents (EDTA and HEDTA) can improve limestone cores permeability during seawater injection and it will prevent any sort of damage specially the formation damage due to brines incompatibility.

Task 4: Testing the Chelating Agent/Seawater Solution Stability at High Pressure and Temperature (100^{o}C and 1000 psi) for Two Days.

Both tasks 1 and 2 will be carried for different chelating agent concentrations (1 to 5% solutions).

4.1 Material/Resources

4.1.1 Fluids

We used a dead crude oil (API=30) for this study from one of the Saudi Arabia fields; the oil composition is shown in **Table 6** (also see Appendix A form more oil properties; Tables 25 and 26). The synthetic brine solutions were prepared by adding different amounts of NaCl, $NaHCO_3$, KC1, $MgCl_2.6H_2O$, $CaCl_2.2H_2O$ and Na_2SO_4 to the distilled water. Two different brine solutions were prepared: 1) formation water (FW) to establish initial water saturation; 2) synthetic seawater (SSW) as an injecting brine solution to displace crude oil. The total dissolved solids (TDS) for FW and SSW is 213,734 and 57,670 ppm, respectively. In addition to these, chelating agents was diluted from original concentration (mainly 40wt %) using prepared seawater. The detailed composition of entire brine solutions are given in **Table 7**. The following chelating agents were used in the study:

- Tetrasodium Ethylenediamine TetraAcetate (Na_4EDTA).
- Biodegradable Chelating Agent (BCA).
- HydroxyEthyleneDiamineTriAcetic Acid (HEDTA).
- Tetra-ammonium Ethylenediamine TetraAcetate (NH_4EDTA).

Table 6 Fluid composition for UTMN crude oil

Component	Moles	Mole%
C5	0.00216	1.23
C6	0.007434	4.23
C7	0.018767	10.67
C8	0.027806	15.81
C9	0.025519	14.51
C10	0.025371	14.43
C11	0.019607	11.15
C12+	0.049211	27.98

Table 7- Composition of Seawater and Formation Brine Used in this Study

Ions	Connate Water	Seawater
Sodium	59,491	18,300
Calcium	19,040	650
Magnesium	2,439	2,110
Sulfate	350	4,290
Chloride	132,060	32,200
Carbonate	0	0
Bicarbonate	354	120
TDS	213,734	57,670

4.1.2 Core plugs

Standard Indiana limestone core plugs were used in the experiments. The porosity of the cores is about 15-21% and the permeability is about 70-100 mD. The core plugs are very homogenous regarding permeability and porosity. They are 3.75 cm in diameter and 5-7 cm in length. The core plugs from the carbonate reservoir has been used to test the low pH BCA solution only. The detailed properties of the core plugs used in this study re given in **Table 8**. CT scan was used at the begging of the core preparation stage to select the best core plugs for the flooding tests.

4.2 Experimental Work

4.2.1 Core Preparation

Core plugs were cut from a single block of Indiana limestone. The cores were 1.5 in. in diameter and 4.5 to 5 in. in length.

Permeabilities to formation brine ranged from 78.94 mD to 185 mD. Porosities were all in the range from 15% to 19. After saturation of a core with formation brine (**Table 5**) using a saturator pressure vessel (**Fig. 13**) connected to a vacuum pump. The pore volume of cores was determined as follows:

- Measure dry weight of the core sample.
- Saturate core plug under vacuum for 5-7 days with field connate water to achieve ionic equilibrium with the core samples.
- Measure wet weight.
- Determine pore volume by weight difference and the density of field connate water at room temperature.

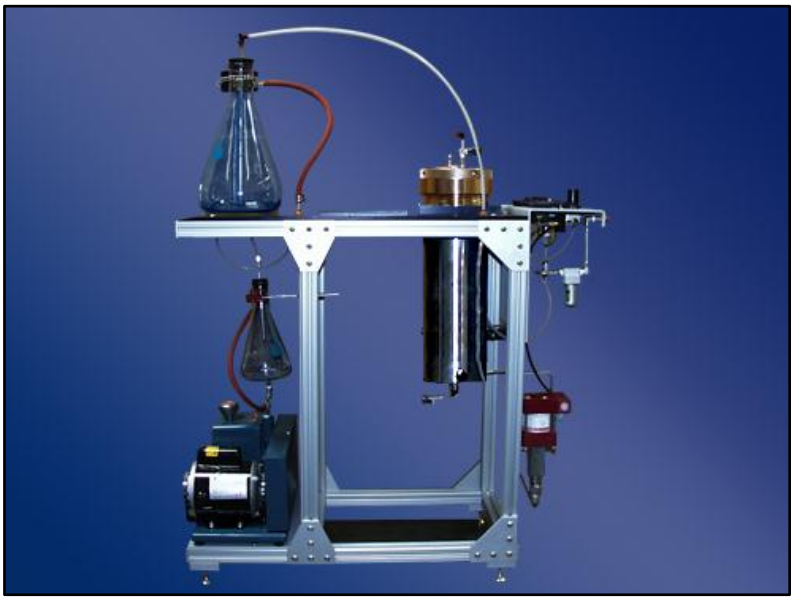


Fig. 13— Core sample saturator.

For each sample, Ionic equilibrium was allowed to be established between the rock constituents and the brine for at least 10 days. Formation water viscosity and density were then measure using the capillary viscometer and the pycnometer respectively; (1.55 cp Viscosity and 1.143 gm/cc density). Then the cores were inserted into a Hassler core holder. The confining pressure was 2500 psi. At least 10 PV of brine were then passed through the sample.

Measurements of brine permeability were made during this stage of core preparation. **Table 8** lists the core properties. The samples were then flooded by oil to achieve initial water saturation using the same flooding system. The last Column in **Table 8** shows the achieved initial water saturation for each sample. In order to have a good interaction between the core plugs and the injected crude oil the samples were kept at 90^{o}C oven for aging for two weeks.

Table 8- Indiana Limestone Core Data.

Core #	Length cm	Diameter cm	Dry Sample Weight gm.	Saturated. Sample Weight gm.	Bulk Volume. cc	Pore Volume cc	Grain Density gm./cc	Porosity %	Permeability mD	S_{Wi} %
H-01	12.27	3.74	292.37	319.24	134.80	23.52	2.63	17.45	101.60	38.04
H-02	12.24	3.74	291.32	320.30	134.47	25.36	2.67	18.86	96.15	42.95
H-03	12.52	3.74	297.07	325.58	137.84	24.95	2.63	18.10	95.09	44.41
H-04	12.67	3.74	300.80	327.97	139.46	23.78	2.60	17.05	160.03	58.49
H-05	12.49	3.75	298.57	322.36	137.73	20.82	2.55	15.12	78.94	43.00
H-06	12.69	3.75	302.74	329.38	139.93	23.32	2.60	16.66	88.90	36.22

4.2.2 Core Flooding Apparatus

The coreflooding apparatus used in this research work is custom designed to perform experiments using up to 12 inches core plugs to evaluate oil recovery using waterflooding or any other type of displacing fluid at reservoir conditions. A schematic diagram of the coreflooding apparatus is depicted in **Fig. 14.** The main components of the apparatus are oven, stainless steel core holder, fluid accumulators, differential pressure array, differential pressure transducer, back pressure regulator (BPR), fractional collector, and confining pressure pump.

The flooding system is capable of handling temperatures up to 150 °C, pore pressures up to 3000 psi, and overburden pressures up to 6,000 psi. Volumes of oil, seawater and chemical solution are supplied from high-pressure floating piston accumulators, operated by external high-pressure Isco pumps. System pressure is maintained by a back pressure regulator (BPR) at the core outlet, and measured by absolute and differential pressure transducers.

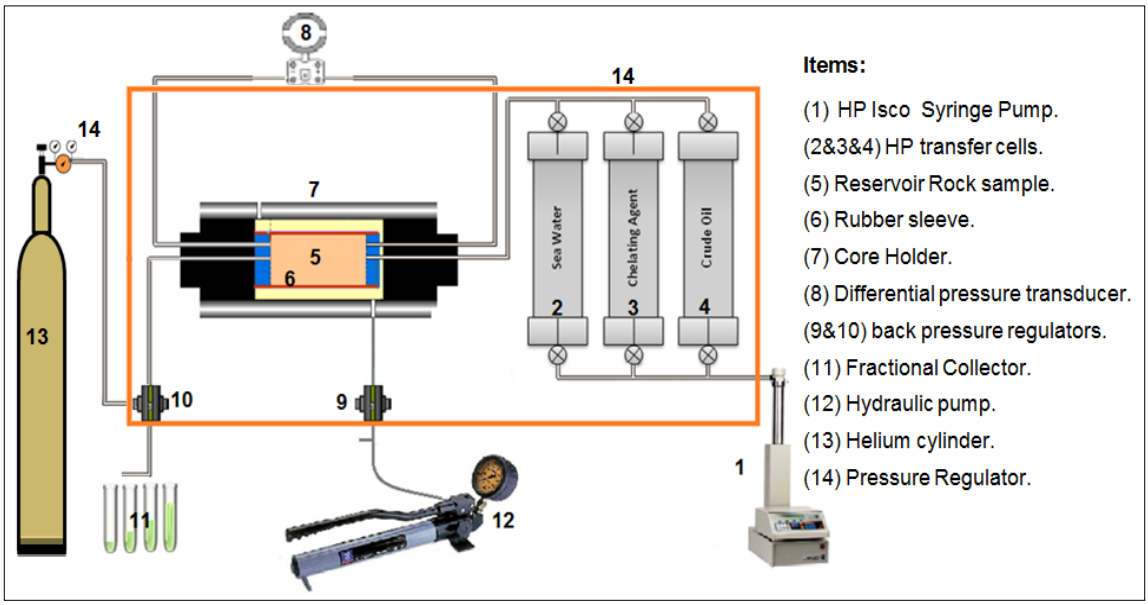


Fig. 14— Flooding Setup used for the study

4.3 Experimental Procedures

The coreflooding apparatus shown before in **Fig. 14** was used to carry out the core flooding tests at reservoir conditions. The experimental procedure followed is described below:

- All accumulators of the coreflooding apparatus were first filled with injected fluids including oil and brines.
- The core plugs were placed into a rubber sleeve, and loaded into the core holder.
- Confining pressure was set to 1,500 psi was maintained on the core by filling the core holder confining annulus with mineral oil.
- The formation brine was used to measure the initial permeability of the core samples using steady state conditions as applied by Darcy law, flow rates of 1, 3, 5, 7 cc/min were used to plot pressure drop vs. flow rate.
- Confining pressure was raised up to constant value of 2500 psi.
- The pore pressure is initiated by setting up the back pressure regulator at 1000 psi.
- Dead oil was flushed through the cores at back pressure conditions to complete fluid saturation.
- The oven was switched on and the temperature was set to the reservoir temperature of 100 °C.
- The pore pressure of the composite was set at reservoir pressure (1000 psi) through the back pressure regulator.
- Conduct seawater flooding while monitoring the amount of oil produced, the pressure drop across the core plug, and the injection rate of the seawater as a function of time.

- The flooding effluent was collected and the IC analysis was done to quantify the concentration of cations (especially Ca^{2+}, Mg^{2+}, and Na^{2+}), and anions (especially SO_4^{2-}) in the effluent samples at different injected pore volumes.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 EOR Core Flooding

5.1.1 Continuous Arabian Gulf Waterflooding

To have a base line for the flooding work and analysis the first flooding was run for a continuous seawater injection under reservoir conditions; **Fig. 15** shows the oil recovery factor by continuous sea injection, it is clear that the main mechanism behind the oil recovery get slow down after 58.53 % recovery.

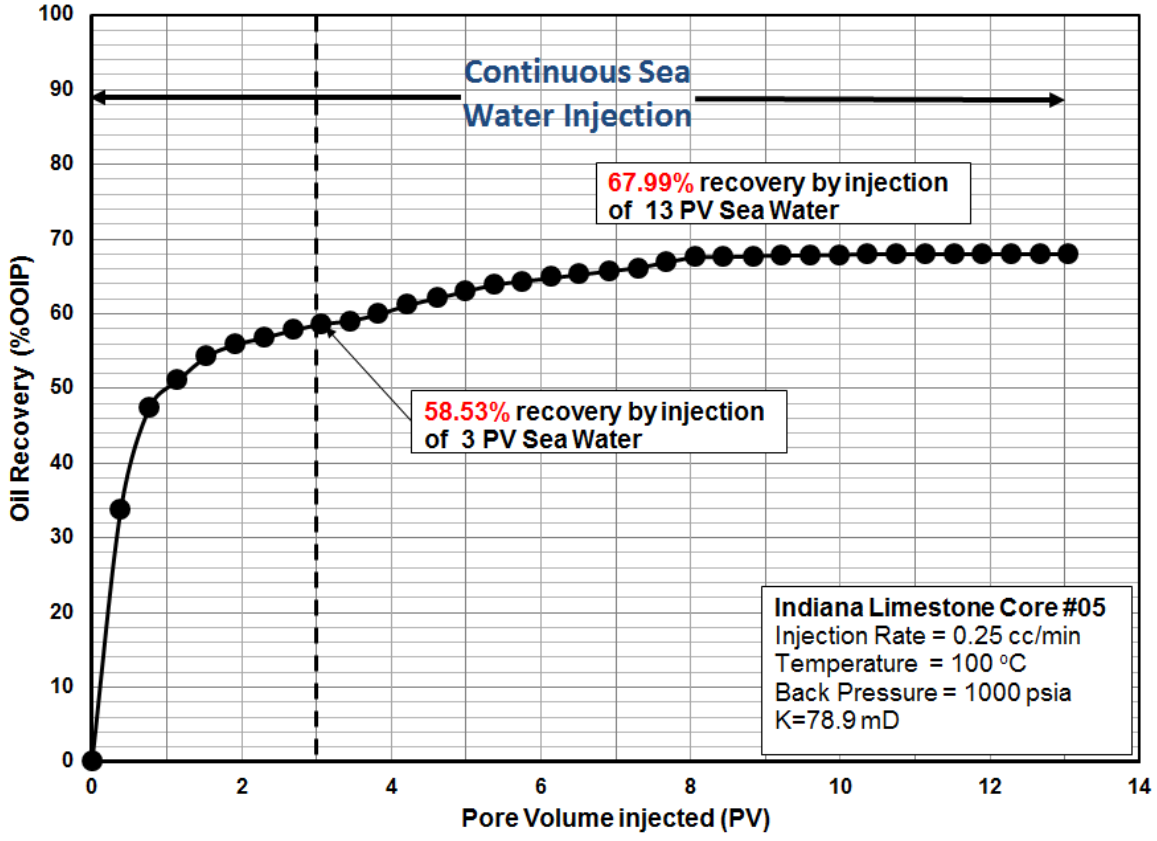


Fig. 15—Oil recovery by continuous seawater injection

Core flooding with seawater will serve as a base for the planned core flooding tests using chelating agents. Ionic chromatography (IC) of the effluent samples for each flooding run for Na^{+}, Ca^{2+}, Mg^{2+}, and SO_4^{2-} ions concentration also will be used. The total achieved recovery factor after injecting about 13 PV of seawater in to core#5 is shown to be 67.99 %. **Fig. 16** shows the IC analysis for the seawater flooding test, it's clear that there is no ion exchange as Ca^{2+} and Mg^{2+} concentrations remained constant in the effluent samples .

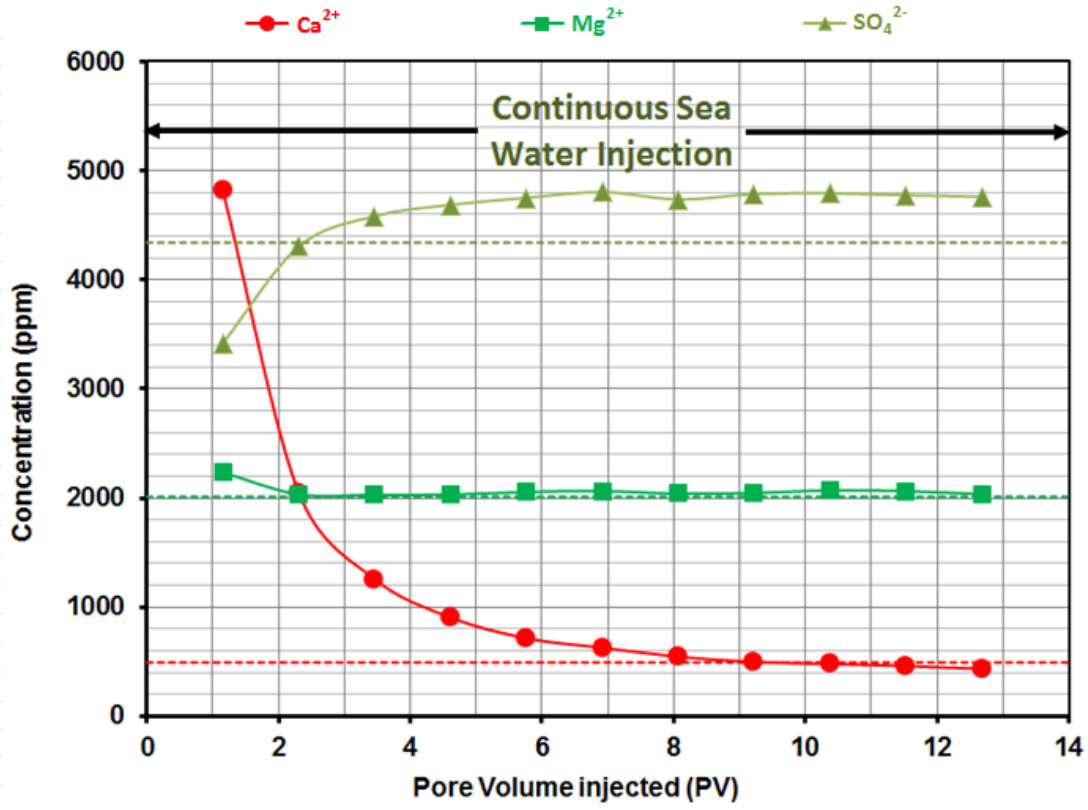


Fig. 16— Concentration profiles for Mg^{2+}, Ca^{2+}, and SO^{4-} (ppm) in the effluent as a function of pore volume injected (PV) for Core #H-06 flooded by continuous seawater.

5.1.2 Seawater injection Followed by 3 wt% EDTA Solution (Exp.2)

During This flooding test 3 wt % NH_4EDTA/seawater solutions (pH=12.2) was used to recover the residual oil behind the injected 3 PV seawater. The recovery curve (**Fig. 17**) shows that the 3 wt % NH_4EDTA can recover only 8.93 % of the OOIP as an additional recovery after injection of about 7 PV which is almost the same recovery if we continue injecting raw seawater. Effluent collected using fractional collector at constant time intervals were analyzed using the Metrohm ion chromatography for Na^+, Ca^{2+}, Mg^{2+}, and SO_4^{2-} ions. The effluent samples were diluted 1000 times with distilled water before the analysis to meet the concentration limits of the equipment.

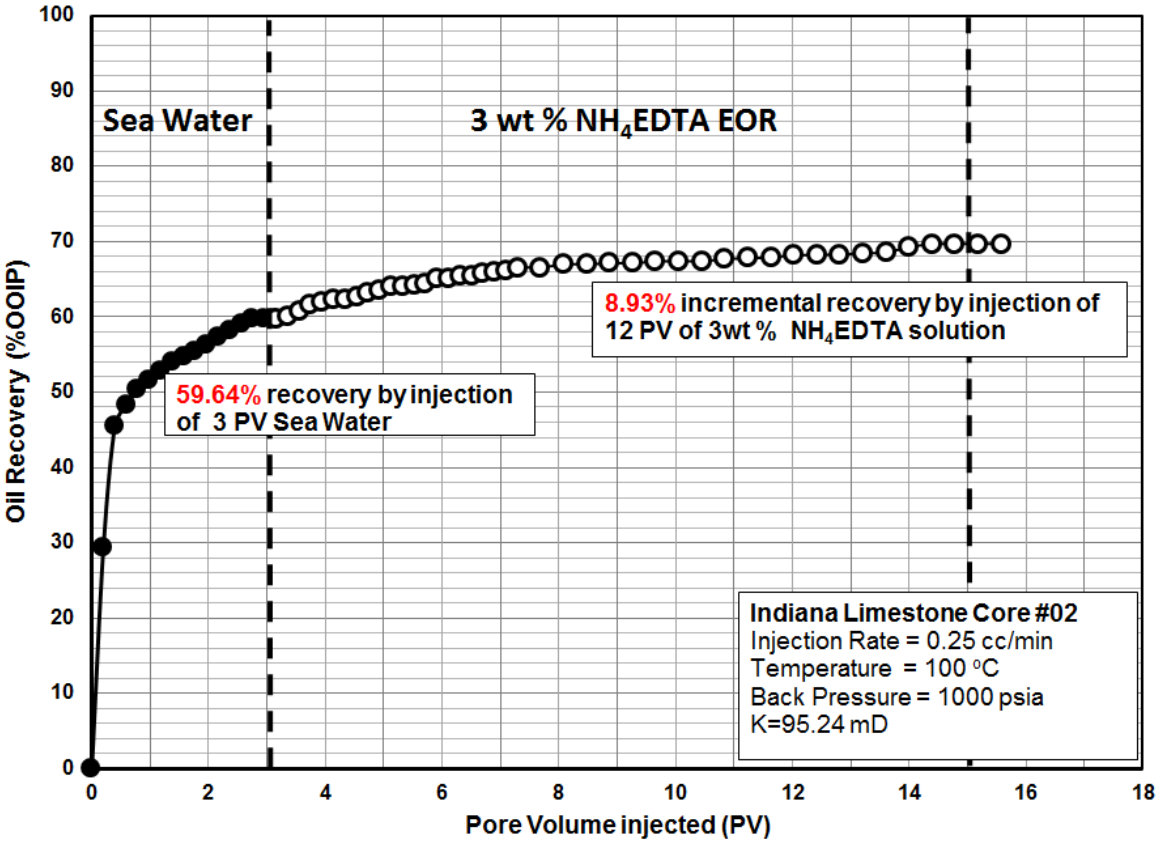


Fig. 17—Oil recovery as a function of pore volume injected (PV) for Core #H-02 flooded by seawater followed by 3wt % NH_4EDTA /Seawater Solution.

Fig. 18 shows the IC analysis for the 3 wt% flooding experiment. It's clear that there is no change in SO_4^{2-} concentration in the effluent and its value is the same as the SO_4^{2-} concentration in the inlet (the dashed lines are showing the concentration of different ions in injected seawater) which means no anhydrite precipitation in the core plug during the flooding test. Also the 3wt % solution did not chelate any more Ca^{2+} from the core matrix which indicates that the dissolution mechanism did not exist to increase the oil recovery. Also, it is clear that the sulfate concentration increased because the 3 wt% EDTA removed the precipitated sulfate by seawater injection and was not able to dissolve calcium from the matrix and the recovery was not increased.

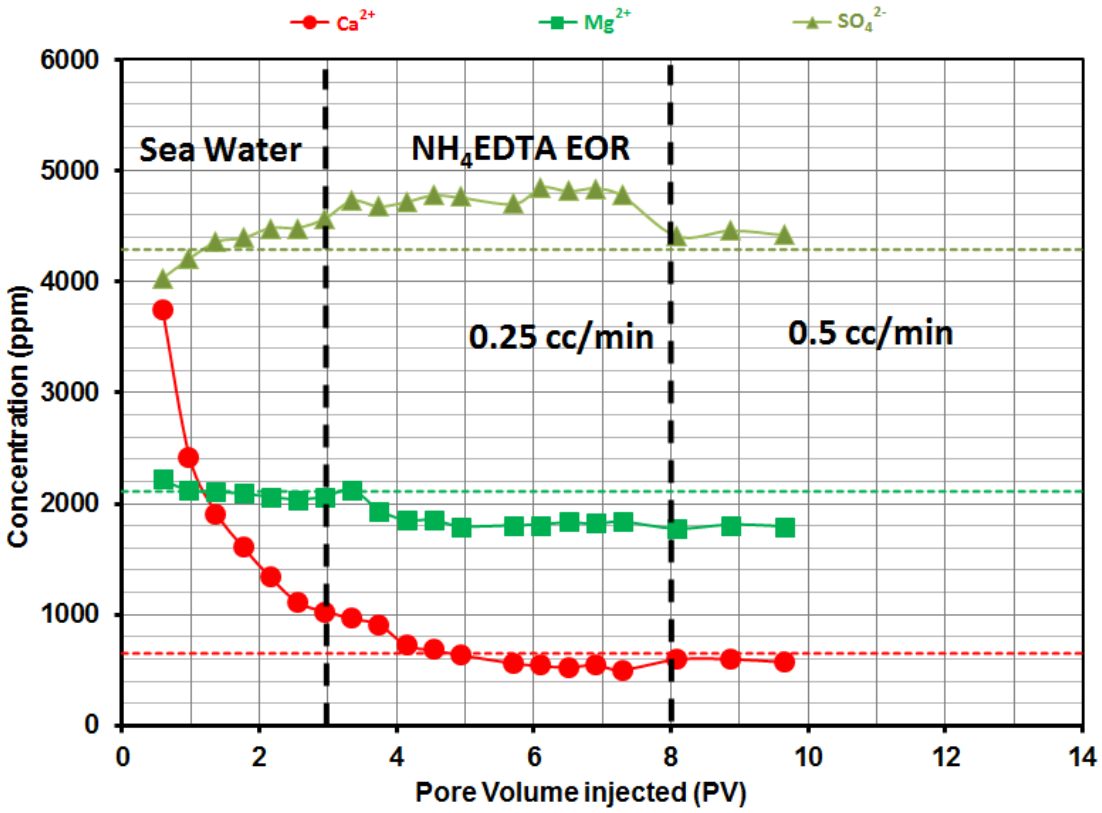


Fig. 18—Concentration profiles for Mg^{2+}, Ca^{2+}, and SO^{4-} (ppm) in the effluent as a function of pore volume injected (PV) for Core #H-02 flooded by seawater followed by 3wt % NH_4EDTA /Seawater Solution (pH=12.2) at $100^{O}C$.

5.1.3 Seawater injection Followed by 5 wt% EDTA Solution (Exp.3)

To test the effect of EDTA concentration on oil recovery, 5 wt % NH_4EDTA/seawater solutions was injected to recover the residual oil after injecting 3 PV of seawater. **Fig. 19** shows that the 5 wt % NH_4EDTA recovered 20.16 % of the OOIP as an additional recovery after injection of about 7 PV. **Fig. 20** shoes the ionic analysis of the effluent collected using fractional collector at constant time intervals using IC analysis. It can be seen from Fig. 20 that most of additional oil was associated with Ca^{2+} chelation from the rock matrix as the Ca^{2+} concentration in the effluent is 600 ppm higher than its concentration in the injected fluid which indicates that rock dissolution was taking place. Dissolution of rock material could be a possible mechanism for the incremental oil recovery increment with EDTA/seawater solution from the carbonate reservoir core plugs at 100°C.

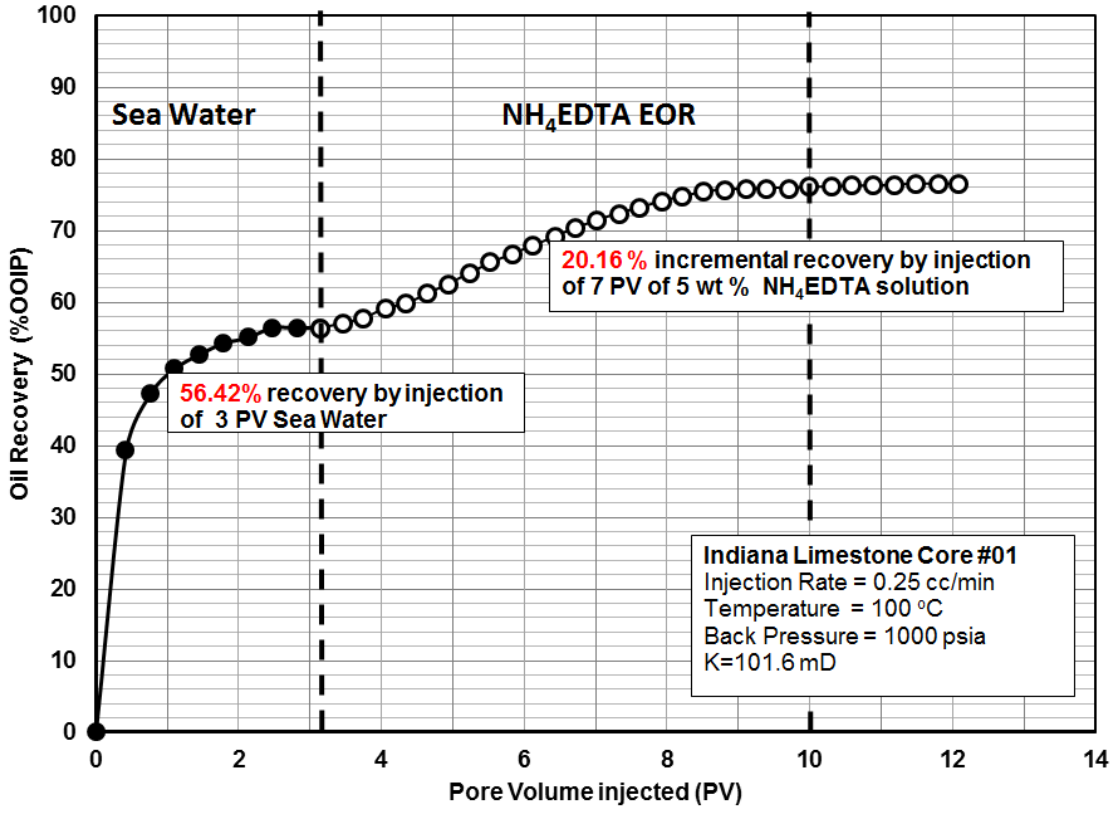


Fig. 19—Oil recovery by seawater followed by 5wt% NH_4EDTA at 100^{O}C.

The IC analysis shows that the 5% EDTA dissolves the precipitated sulfate plus increasing the recovery, the extra 2 wt% gives the increase in recovery.

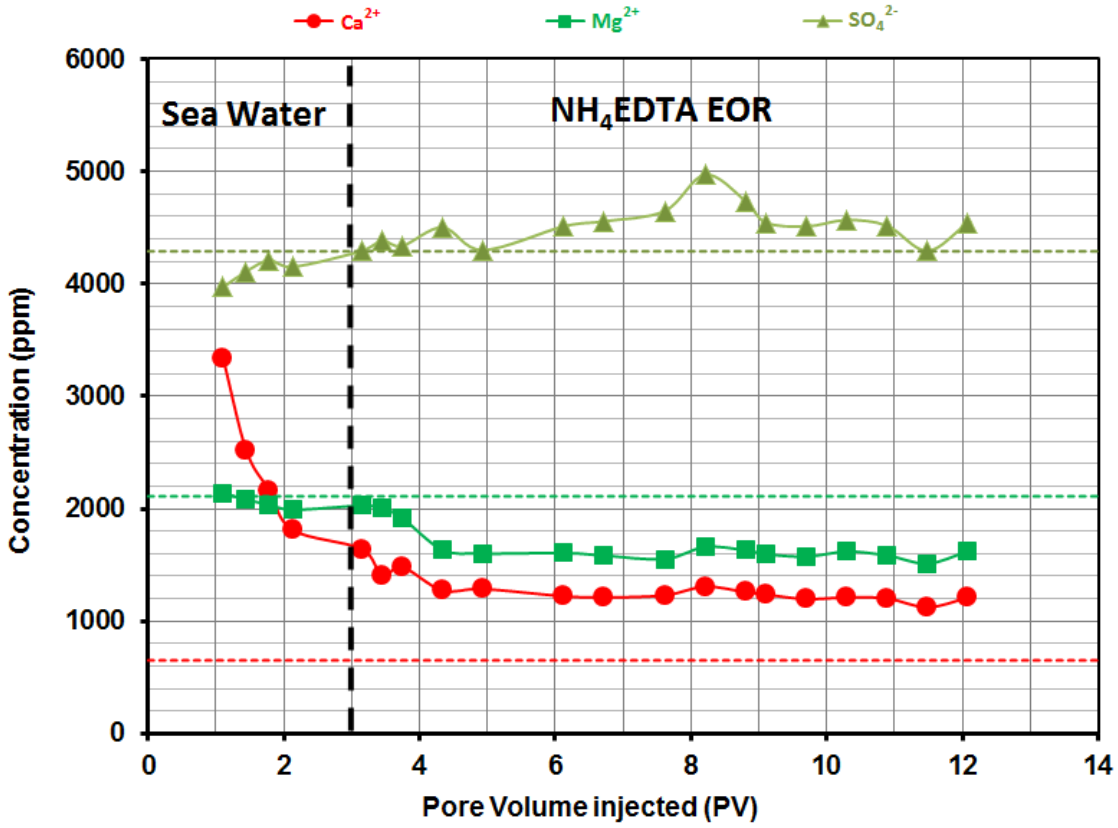


Fig. 20—Concentration profiles for Mg^{2+}, Ca^{2+}, and SO^{4-} (ppm) in the effluent as a function of pore volume injected (PV) for Core #H-01 flooded by seawater followed by 5wt % NH_4EDTA /Seawater Solution (pH=12.2) at $100^{O}C$.

Fig.21 is comparing the oil recovery when EDTA solution was injected at connate water saturation to continuous seawater injection. It is clear that when 5 wt% of EDTA is injected at S_{wi} it will result in an earlier recovery increase over seawater. In case of continuous sea EDTA injection after injecting 3 PVs the recovery factor is about 72 % compared to 58 % in case of continuous seawater injection. The difference between the two curves is about 10% incremental recovery at the end of flooding as shown in the below figure.

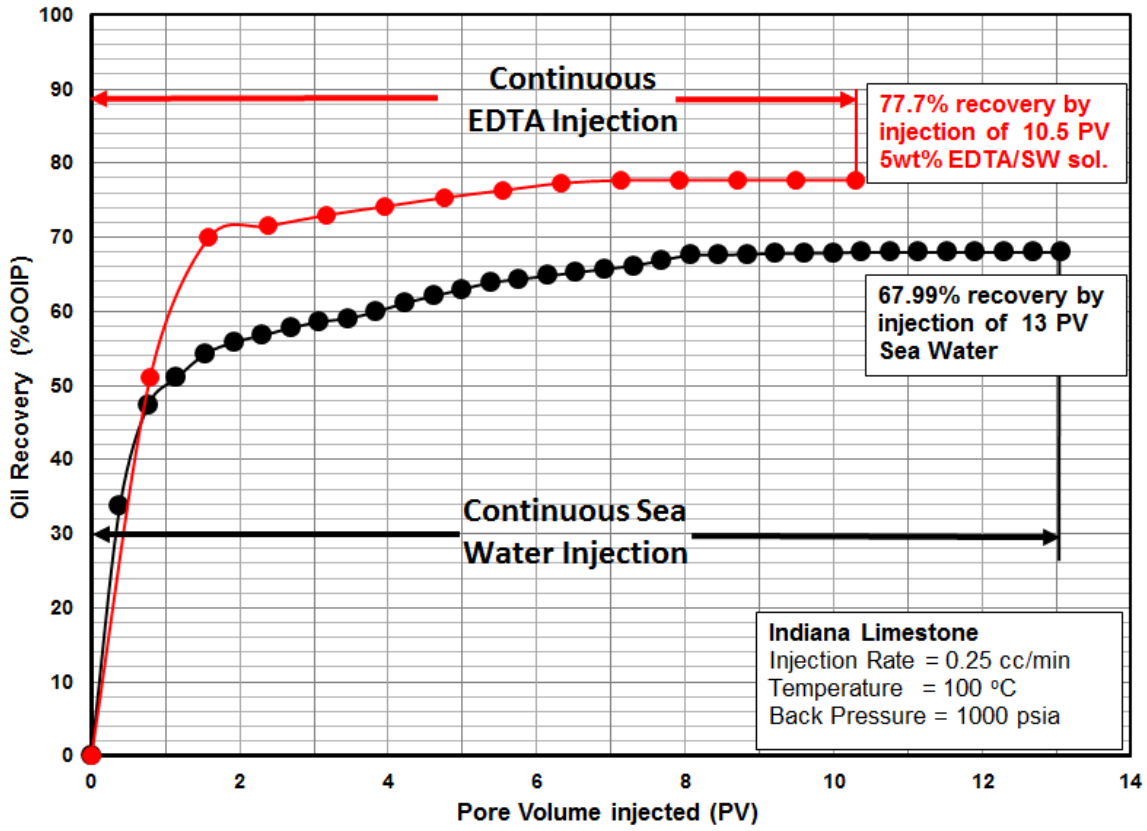


Fig. 21—Continuous Seawater vs. continuous EDTA/Sw injection

When Continuous 5 wt% EDTA flooding is compared to seawater flooding followed by 5 wt% EDTA injection **(Fig.22)**, although both of them dive the same recovery factor at the end of flooding test but 5 wt% EDTA injected at S_{wi} showed an earlier increased recovery factor (72% compared to 56% in case of seawater injection).we can conclude out of **Fig.22** that either starting with seawater injection followed by EDTA solution or starting with EDTA solution will end up with the same recovery but in the second case we can have an earlier increase in recovery due to the increased time of interaction of EDTA with the core sample.

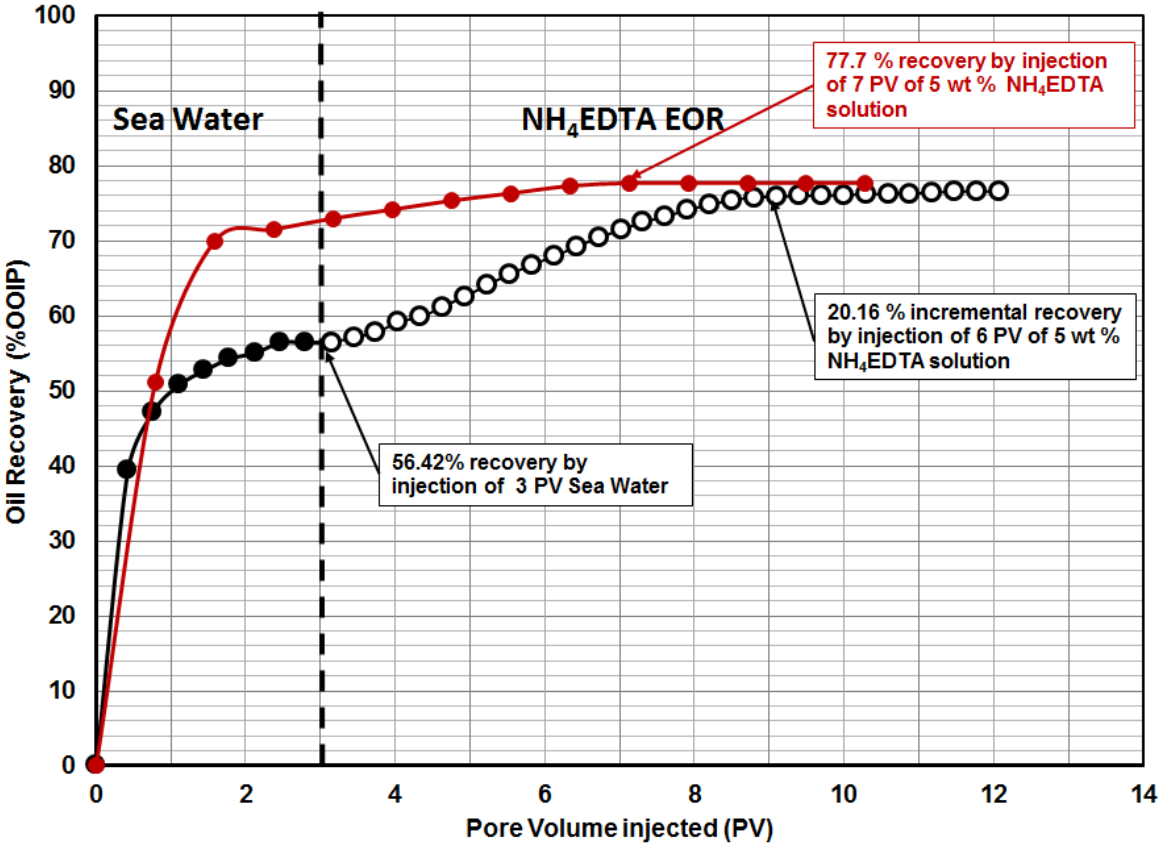


Fig. 22—Continuous EDTA/SW vs. seawater followed by EDTA/SW injection.

5.2 In-Situ CO_2 EOR in Carbonate Reservoirs

The coreflooding experiments were performed using Indiana limestone cores 6 in. length and 1.5 in diameter. H_2Na_2EDTA (pH = 4.5), H_3HEDTA (pH=2.5) and Na_4EDTA (pH = 12) chelating agents **Fig. 5**) were used to generate CO_2 in-situ (the generated CO_2 can be followed by seawater or continuous injection of high pH chelating agent to get more oil recovery). The concentration of the chelating agents used was 5 wt% therefore, no other additives are required to protect against corrosion.

The experiment was performed at 100^oC and 0.25 cc/min injection rate. The core was flooded first by seawater which recovered 58% of the initial oil from the core, i.e., 42% of the oil still inside the core. One pore volume of 5wt% H_3HEDTA (pH=2.5) was injected and it recovered 34% additional oil from the oil in place or 81% from the residual oil (**Fig. 23**). It should be noted that one pore volume of 5 wt% H_3HEDTA produced enough amount of CO_2 to recover more than 80% of the residual oil. The same in **Fig. 24** we used H_2Na_2EDTA at pH 4.5, continuous injection of this chemical increased the oil recovery more than 90% from the initial oil in place. H_2Na_2EDTA was not powerful as H_3HEDTA in producing CO_2; therefore, more volumes of H_2Na_2EDTA will be injected to recover additional oil equal to that recovered with H_3HEDTA. This process can be controlled by proper design of the concentration, pH, and chelating agent type to maximize the oil recovery as much as possible. CT scan for the EOR#02 core is shown in **Fig. 25** with comparison between both the high pH and low pH flooded cores in **Fig. 26**, as shown a dominating wormhole was generated in the core due to the interaction between the low pH EDTA and the calcite matrix. **Table 9** shows the core properties of the Indiana limestone samples used in the flooding test shown in **Fig. 23** and **24**.

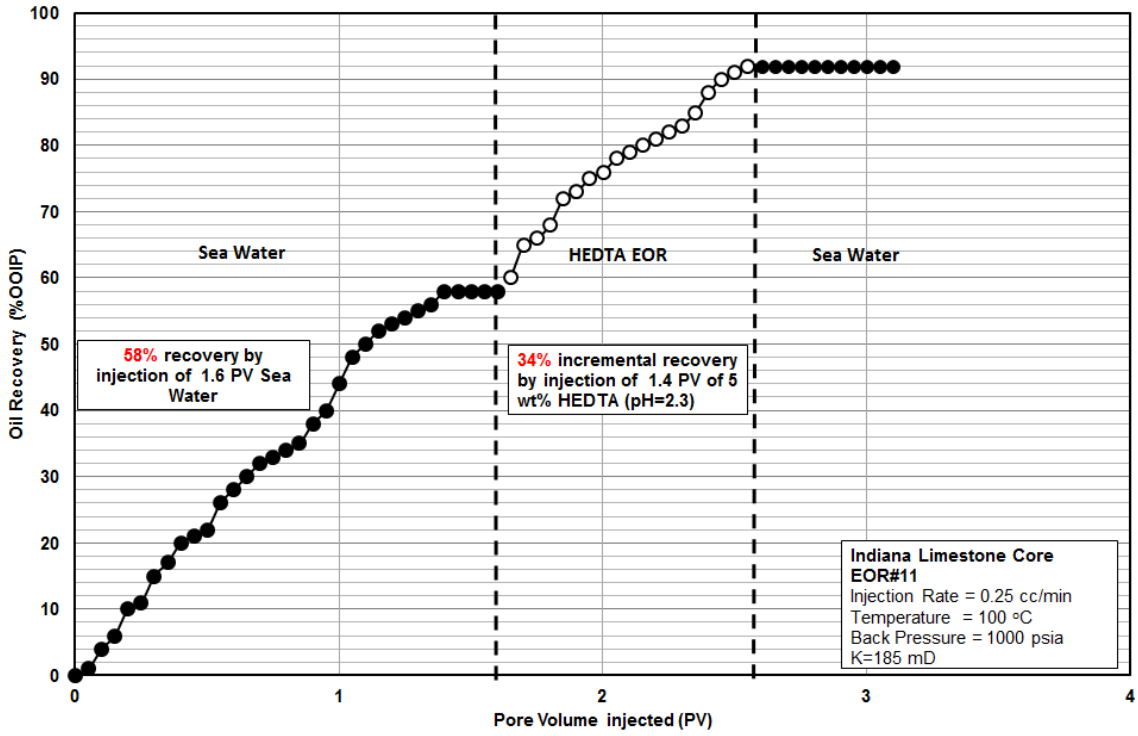


Fig. 23—Oil recovery by the in-situ generation of CO_2 using H_3HEDTA (pH=4.5) from core#11.

Table 9- Properties of the core samples used for the in-situ CO_2 flooding tests

Core #	L (cm)	D (cm)	Dry Wt. (gm)	Bulk Vol. (cc)	Saturated Wt. (gm)	Porosity (%)	Perm (mD)	Pore Vol (cc)
EOR-1	15.000	3.720	347.53	163.03	383.45	19.38	70	31.59
EOR-2	15.000	3.720	347.42	163.03	383.58	19.51	70	31.80
EOR-11	15.000	3.720	347.53	163.03	383.45	19.38	185	31.59

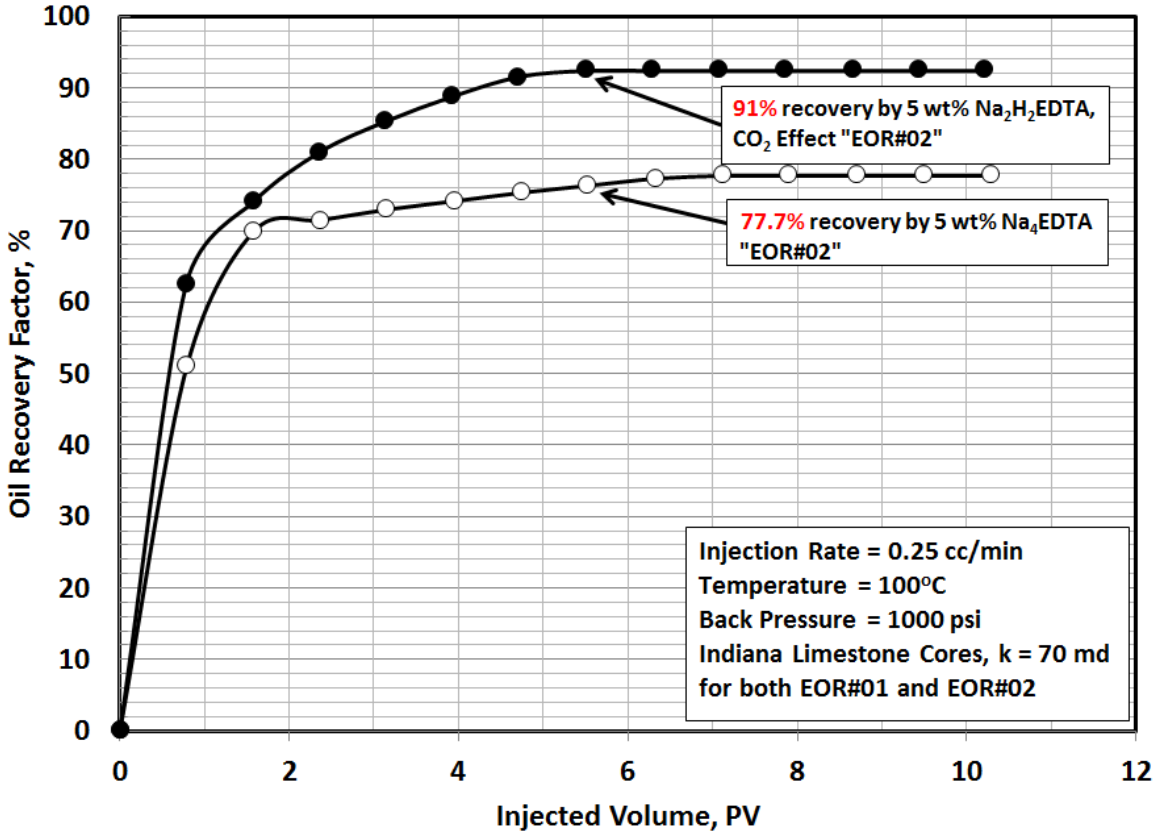


Fig. 24— Oil recovery by the in-situ generation of CO_2 using H_2Na_2EDTA (pH=4.5; EOR#02) vs. Oil recovery using Na_4EDTA (pH=12; EOR#01).

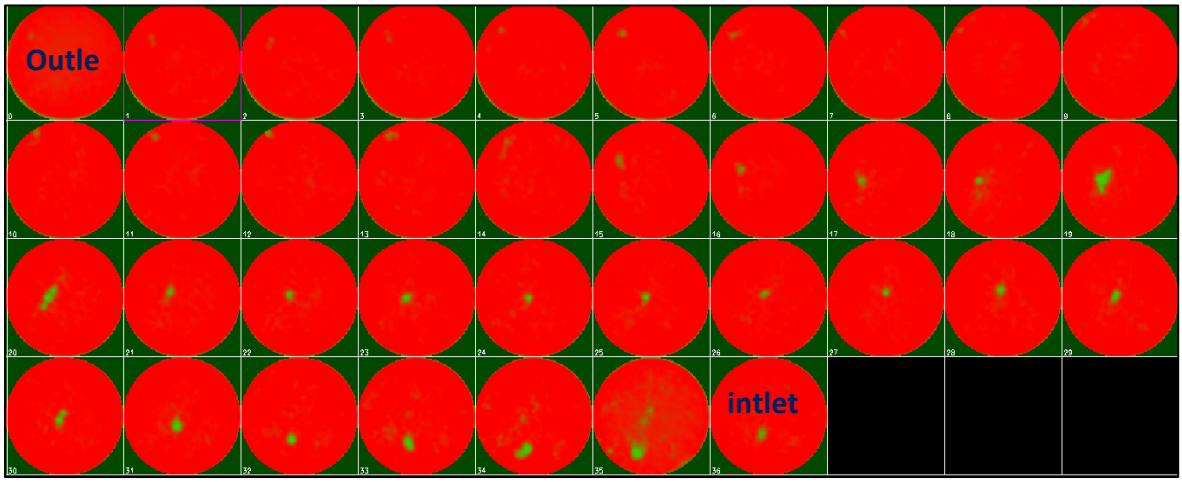


Fig. 25— CT scans of core # EOR#02 after low pH Na_2H_2EDTA solution injection.

Fig. 26— Wormholes created in the Low pH EDTA flooded Core (pH = 4.5; right core) Compared to the High pH EDTA flooded one (pH = 12; left core).

5.3 Pressure Maintenance Using Raw Seawater Injection Using Chelating Agent Solutions

5.3.1 Effect on brine saturated limestone permeability

The case where water injection (seawater, river, aquifer, or produced water) is used for pressure maintenance and sweep, the mixing of incompatible brines can lead to the formation of sulfate scales when the injected water contains sulfate ions (Mackay and Jordan, 2005). In this section the results from core flooding performed on 213 kppm brine saturated Indiana limestone using different concentrating of high pH EDTA and HEDTA will be shown. The aim of this section is to show that injection of seawater having chelating agents for EOR or pressure maintenance purposes will prevent the formation damage that might take place during traditional seawater injection.

Fig. 27 and 28 show the effectiveness of using EDTA, and HEDTA chelating agents in preventing sulfate scale precipitation and enhancement of core permeability in Indiana limestone cores. EDTA was the best chelating agent in preventing the damage and enhanced the core permeability. EDTA was able to increase core permeability from 80 mD to 100 mD when injected in 5wt% with seawater, and from 83mD to 177mD when injected in 10 wt% with seawater. Generally, EDTA, and HEDTA chelating agents at high concentration (10 wt %) performed better because their high chelation ability of calcium. **Fig 29** shows the performances of different concentrations of EDTA chelating agents in limestone cores. EDTA at 1 wt% concentration was able only to chelate the calcium from the formation brine and the seawater. Increasing the concentration to 5 and then 10 wt% made the EDTA chelating agent more powerful and it was able to dissolve calcite in carbonate cores.

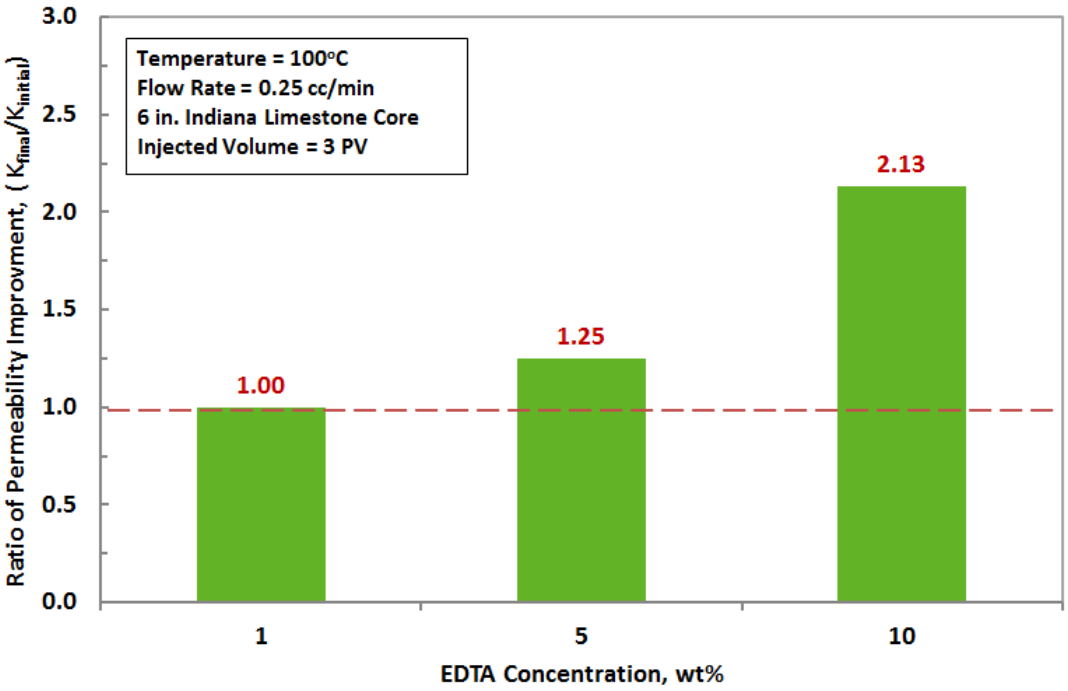


Fig. 27—Improvement in permeability in Indiana limestone cores using different concentration of EDTA/pH = 11.

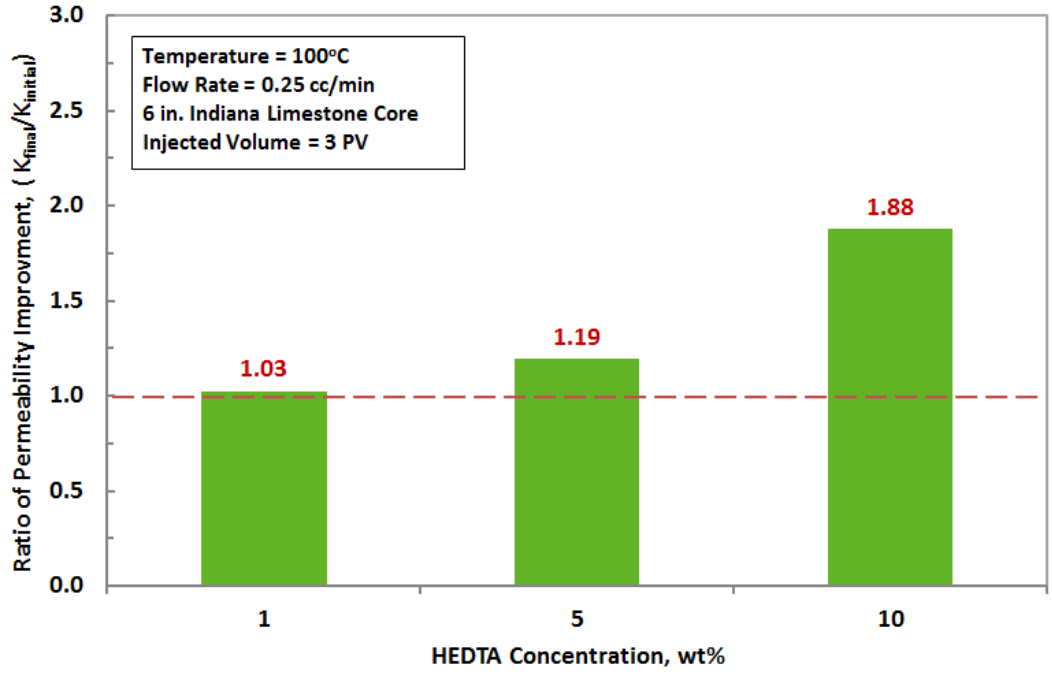


Fig. 28— Improvement in permeability in Indiana limestone cores using different concentration of HEDTA/pH = 11.

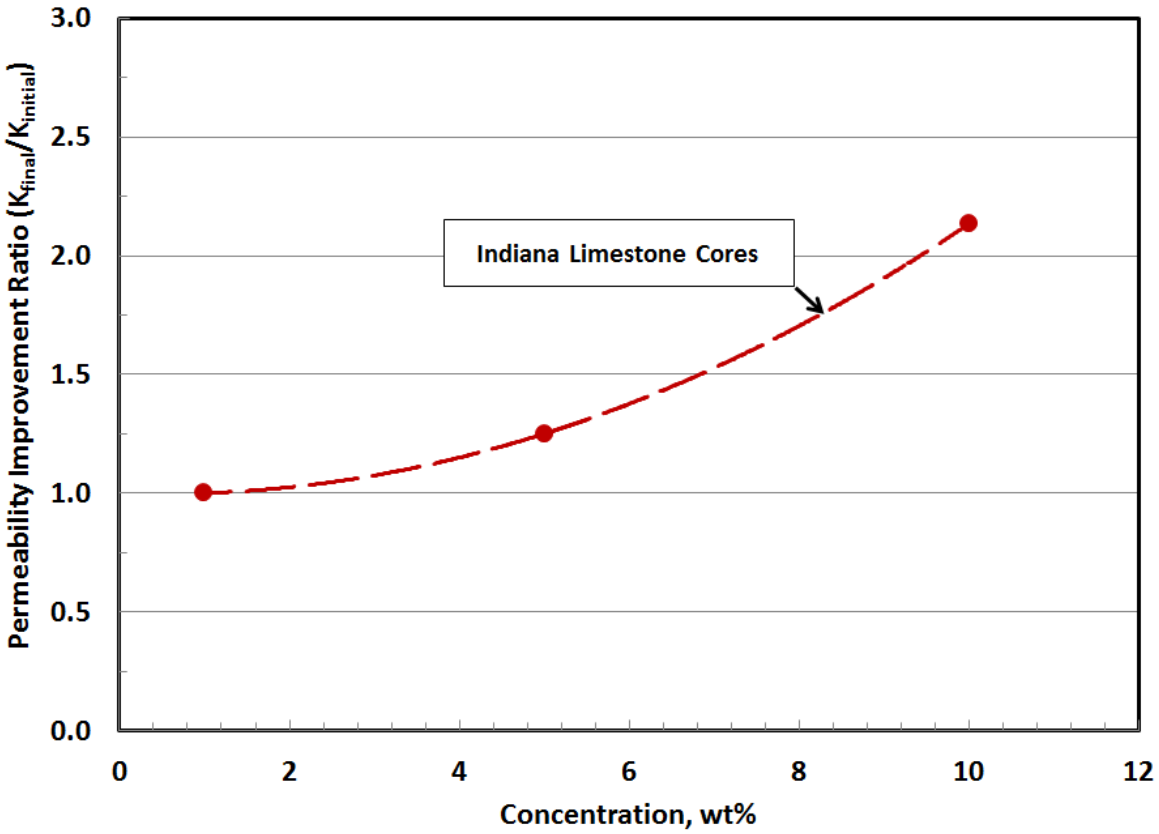


Fig. 29— Improvement in permeability using different concentration of ETDA/pH = 11 in Indiana Limestone cores.

5.3.2 Using HEDTA Chelating Agent in Seawater compared to Raw Seawater and LowSal Water Injection.

Fig. 30 shows the effect of using HEDTA solution to prevent the calcium sulfate scale precipitation in Indiana limestone cores when low salinity seawater injection was used. The final concentration of HEDTA was obtained from an initial concentration of 40 wt% and it was diluted to 20 wt% using low salinity seawater having a composition shown in **Table 10**. The calcium sulfate precipitation highly damaged the core during seawater injection because of the high sulfate content. Diluting the seawater reduced the sulfate concentration from 4290 ppm to 1073 ppm. Comparing the ratio of calcium sulfate in the low salinity and high salinity water, the factor of dilution for sulfate is 4 which is the main source of damage. Naturally we should expect the same in calcium sulfate precipitation reduction, which is not the case.

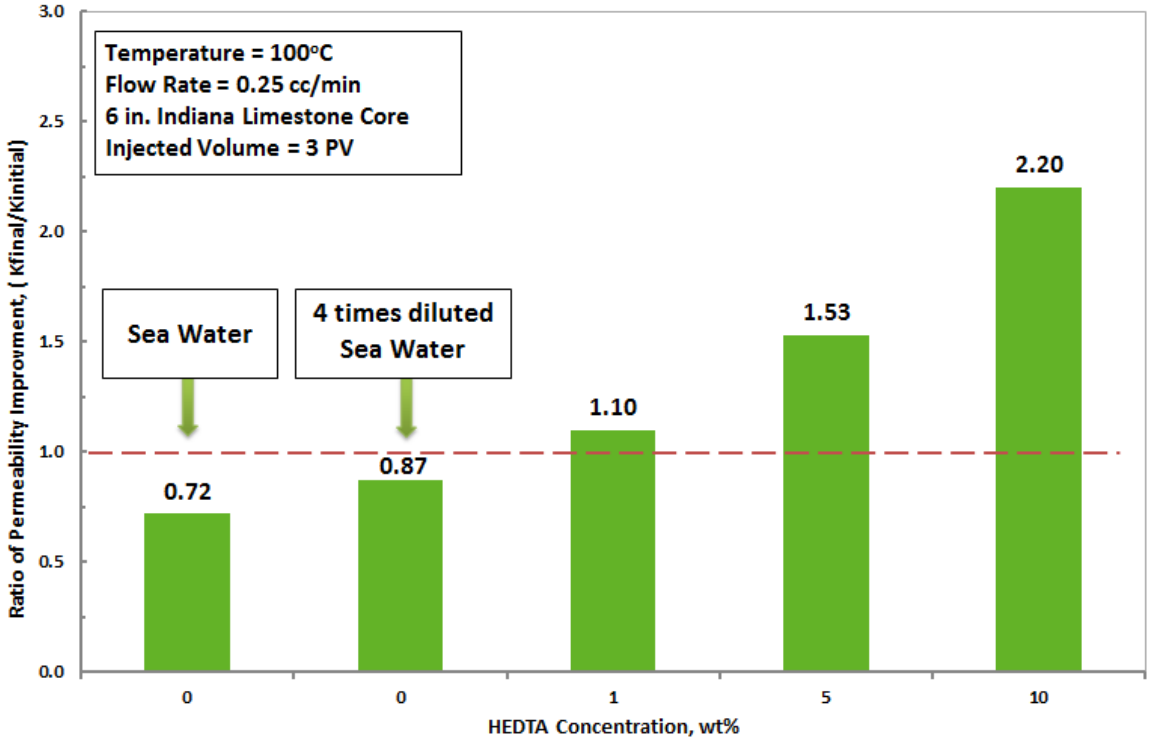


Fig. 30— Improvement in permeability using different concentration of HETDA/pH = 11 in Indiana limestone cores using low salinity water injection.

Table 10- Low Salinity Water Composition (4 times diluted seawater).

Ions	Concentration (ppm)
Sodium	4,575
Calcium	163
Magnesium	528
Sulfate	1,073
Chloride	8,050
Bicarbonate	30
TDS	14,418

The sulfate concentration of 4290 ppm caused 28% loss in the core permeability, reducing the sulfate concentration to 25% of its original concentration should reduce the damage from 28% to 7%. The damage in the low salinity, low sulfate content seawater was 13% almost half the high sulfate content in seawater. Diluting seawater affects the solubility of calcium sulfate. Decreasing sodium chloride concentration decreases the solubility of calcium sulfate and more sulfates can precipitates in a rate more than the high salinity seawater. Recuing sodium concentration enhanced the performance of HEDTA in preventing calcium sulfate precipitation more than the case of seawater. This can be attributed to the high stability of HEDTA in low salinity water and also it was reported before that sodium chloride decreases the chelating ability of HEDT/EDTA solution (Mahmoud et al. 2011c). Reducing sodium chloride concentration allowed the HEDTA to chelate more calcium from the solution and from the rock; therefore, the permeability enhancement was higher in case of HEDTA diluted with low salinity water than that diluted with high salinity seawater.

5.3.3 Effect of pH on the Compatibility between Chelating Agents and Seawater

During this study I found that Chelating agents' compatibility with seawater is a strong function of pH value. **Table 11** and **Fig. 31** show the effect of EDTA pH on the compatibility of EDTA and seawater. The five solutions were prepared from an initial solution of H_2Na_2EDTA of pH value 4.36. Potassium hydroxide was used to increase the pH. As shown in Fig. 31 there was a white precipitate in the first three solutions (pH = 4.36, 5.26, and 6.34), XRD analysis showed that it is an organic precipitate with slight fraction of calcium sulfate. Increasing the pH value to 7.2 made the EDTA compatible with seawater and no precipitation was observed. EDTA cannot be used with seawater at low pH values; it should be used at pH values greater than 7 if there is an essential need to mix it with seawater. EDTA with de-ionized and fresh water did not precipitate at all pH values starting from 4.36.

Table 11- The pH measured for the 5 solutions shown in Fig. 26.

Solution	EDTA Concentration, wt%	pH
1	5	4.36
2	5	5.26
3	5	6.34
4	5	7.20
5	5	8.44

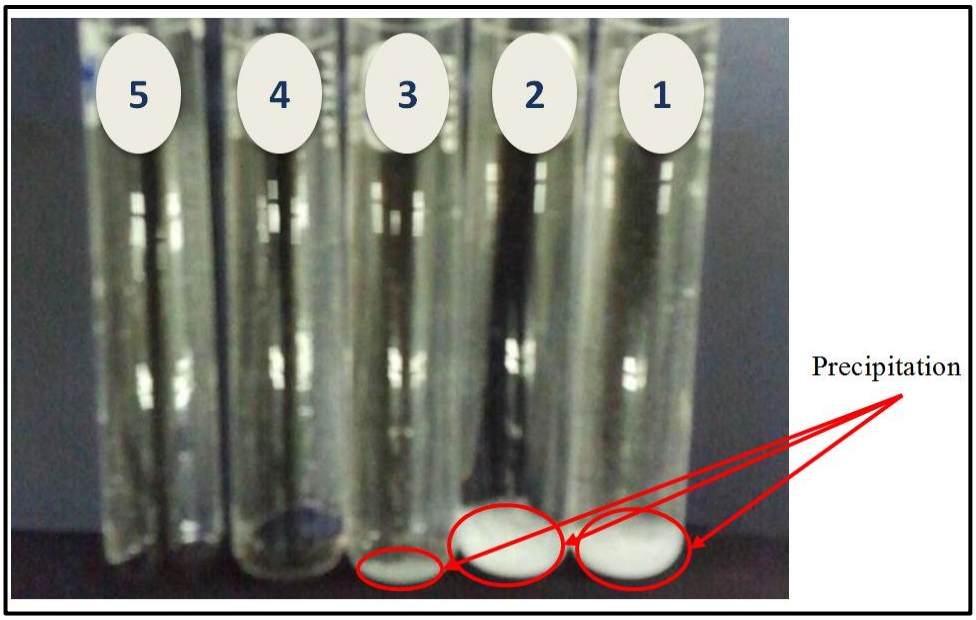


Fig. 31— Effect of pH on EDTA/seawater solution compatibility at room temperature.

This performance of low pH EDAT with seawater lead us to look for another low pH chelating agent compatible with seawater, and having the following features:

- Capable of In-situ CO_2 generation during EOR flooding processes.
- Better rock stimulation due to the higher chelation ability of the chemical in addition to the hydrogen attack.
- Compatible with seawater to prevent any source of damage.

5.3.4 Low pH BCA compatibility with seawater

Biodegradable Chelating Agent (BCA) a newly developed environmentally friendly chelate (**Fig. 32**) was selected for testing it's computability with seawater at different concentrations. Different BCA solutions were prepared in different concentrations using seawater and the pH range is shown in the **Table 12.** BCA at different concentrations was soluble in seawater at room temperature. The solutions were observed on a daily basis for one week and there was no precipitation in all the solutions as shown in **Fig.33**. This was compared to the solubility of EDTA at pH 4.3 and 6.27, at both pH values EDTA. It was observed that phase separation took place after 2 minutes when diluted with seawater and this can be seen from **Figs. 34** to **36**.

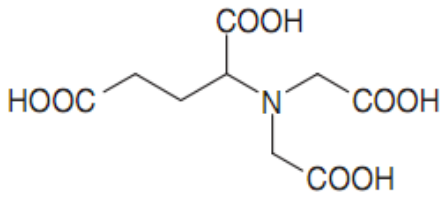


Fig. 32— Biodegradable Chelating Agent (BCA)

Table 12- Prepared BCA/Arabian Gulf seawater solutions

GLDA Initial Concentration = 40 wt% pH= 3.73				
Solution #	**Solution wt%**	**GLDA (gm)**	**Sea water (gm)**	**pH**
1	**0.8**	**0.8**	**39.2**	3.42
2	**4**	**4.0**	**36.0**	3.31
3	**8**	**8.0**	**32.0**	3.31
4	**16**	**16.0**	**24.0**	3.38
5	**24**	**24.0**	**16.0**	3.48
6	**32**	**32.0**	**8.0**	3.56

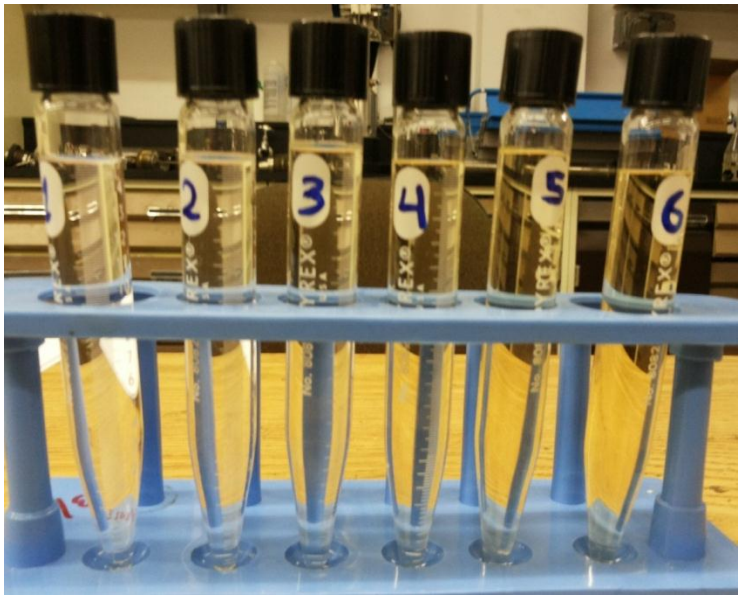


Fig. 33— BCA/seawater different concentration Solutions day 1.

Fig. 34— 5 wt % Low pH Na_2HEDTA (Tube#7) Compared to BCA solutions.

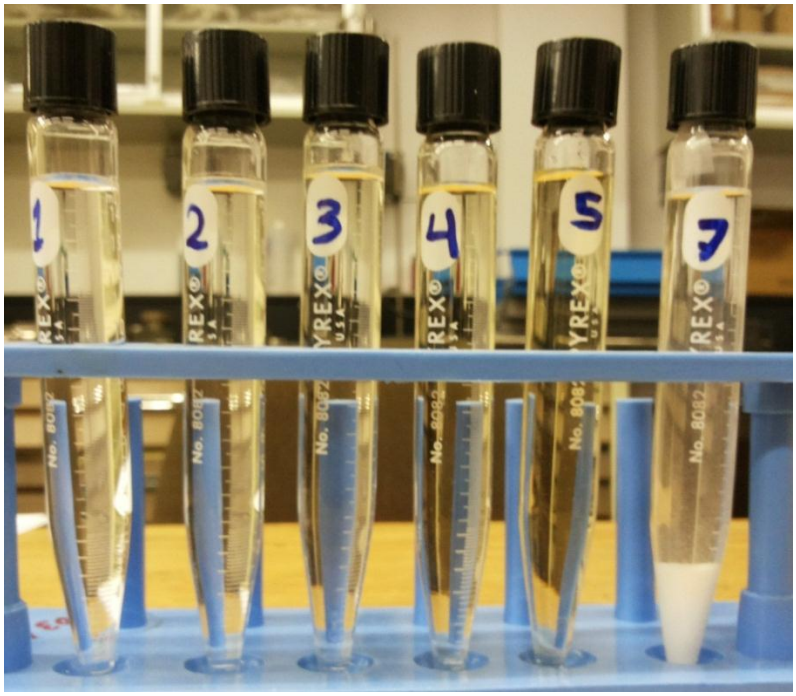


Fig. 35— 5wt% Low pH Na_2HEDTA (tube#7) Compared to BCA after less than 2 minutes

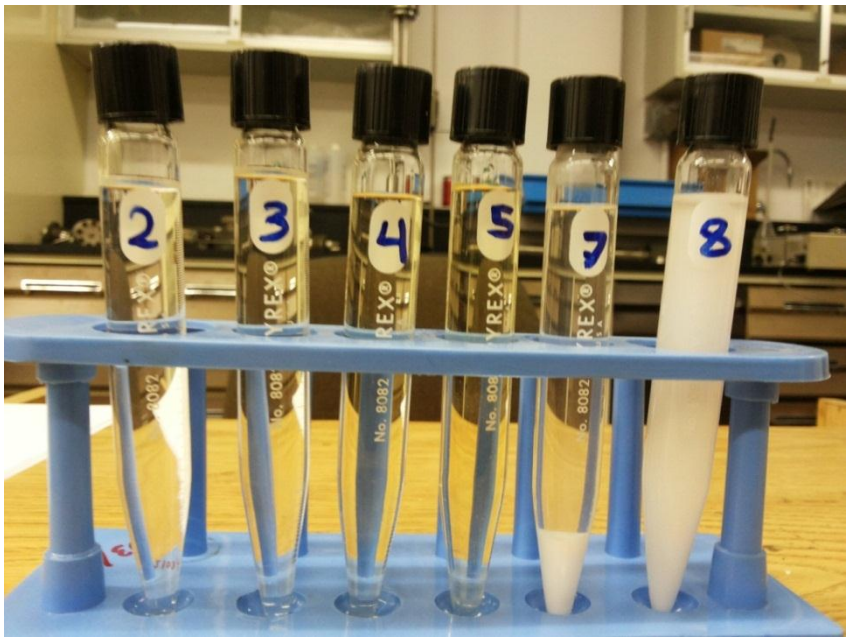


Fig. 36— BCA (pH=3.73; tubes 2-5), Na_2H_2EDTA (pH=4.3 in tube#7, and pH=6.27 in tube#8)

5.3.5 Low pH BCA Stability Test

The stability test was done to ensure the compatibility of the low pH BCA with seawater after interacting with the calcite rock and chelating calcium cations. **Fig. 37** depicts the steps of the stability test done for the BCA seawater solution.

Two concentrations (20 and 15wt %) of BCA diluted with seawater were tested. After applying pressure and temperature on the filtrate the 20wt% solution showed a precipitate at 1000 psi and 100^{o}C indicating that the 20 wt% solution concentration cannot be used for in-situ CO_2 generation in carbonate reservoirs while the 15wt% solution was stable up to a pressure of 5000 psi pressure at 100^{o}C. **Fig. 38** and **39** show different filtrates before and after applying HP/HT conditions. **Table 13** shows the IC of the reaction filtrate for both 20 and 15 wt% BCA solutions, the 15 wt% chelated about 15092 ppm Ca^{2+} as the initial Ca^{2+} concentration in the used seawater was 495 ppm, while the 20 wt% chelated about 16755 ppm Ca^{2+}.

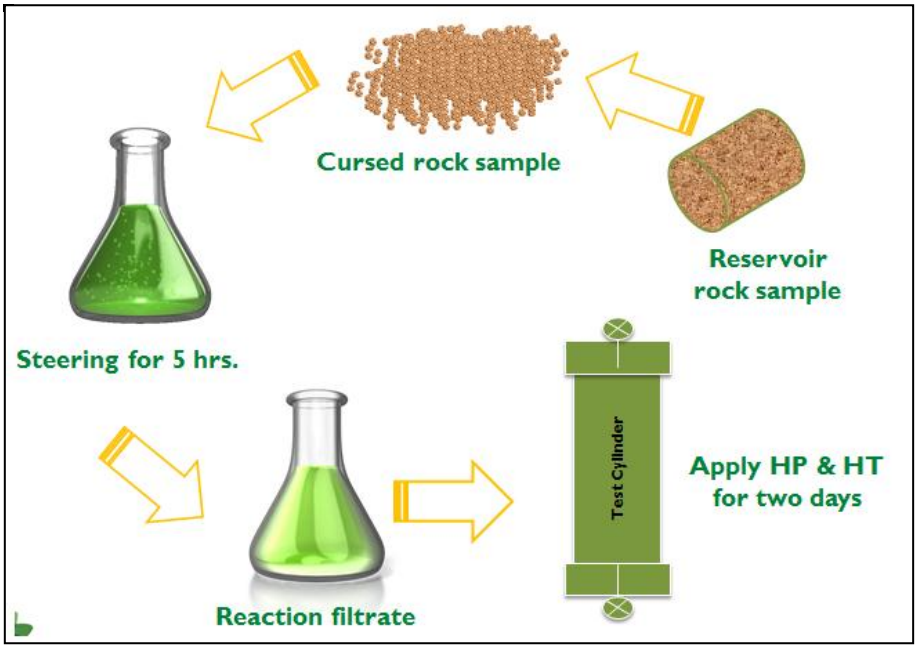


Fig. 37— Stability test of BCA (pH=3.73)

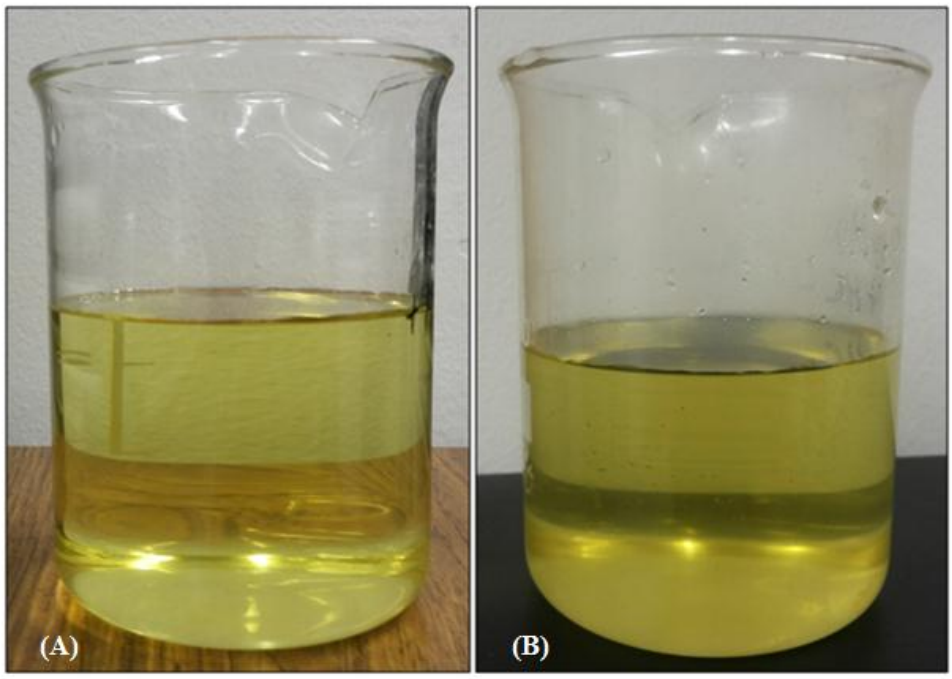


Fig. 38—(A) 15 wt% BCA Reaction filtrate solution in room temperature compared to **(B)** 15 wt% BCA Reaction filtrate solution after 48 hours heating at 100°C and 1000 psi. The solutions stayed in the same picture 4 days after taking it out from the oven.

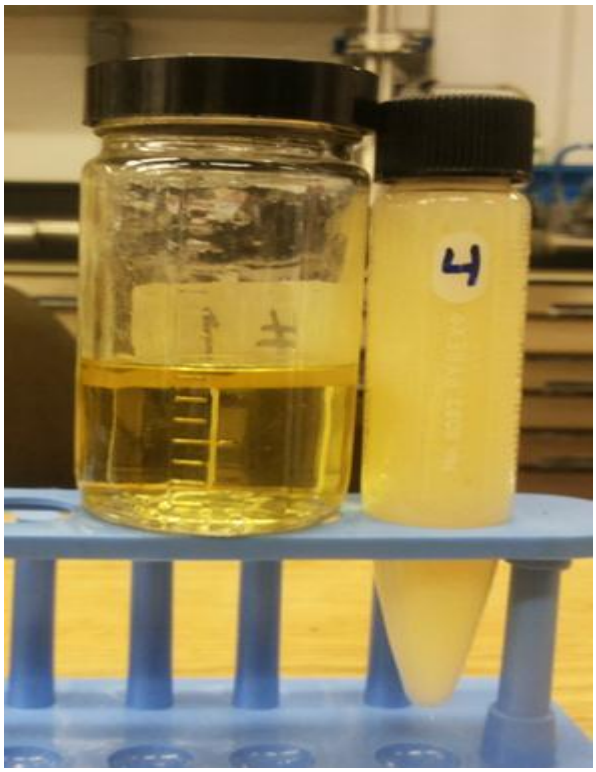


Fig. 39—20 wt% BCA solution after 48 hours heating at 100°C and 1000 psi (the right photo). This experiment repeated twice and the same results were obtained.

Table 13- IC of the filtered 15 and 20 wt% BCA/Seawater after steering with Calcite rock.

Con.	Na^+	Ca^{2+}	Cl^-	SO_4^{2-}	K^+	Br^{2+}
15%	42018.5	16397	22095	3364.5	56	346.5
20%	43425	17247	18541	3286	145	637
Seawater	18300	650	32200	4290	-	-

5.3.6 Core flooding Experiment

Actual carbonate core sample with the specification listed in **Table 14** was used for the coreflood experiment. The experiment was performed using 15 wt% BCA prepared from initial concentration of 40 wt% using synthetic Arabian Gulf water. The experiment was performed at 100^{o}C using 0.5 cc/min injection rate, and 1000 psi back pressure; the overburden pressure was kept constant at 1500 psi. The core and fluid were heated up in the oven over night before the flooding experiment was performed. The core permeability was 5 md, **Fig. 40** and **41** show the core inlet and outlet respectively after flooding by BCA, no washout was observed and the core integrity was maintain after the flooding as shown in **Fig. 42**. **Fig. 43** shows the pressure drop across the sample during the flooding experiment. The 15 wt% solution was able to stimulate the core as shown by the generated wormhole which breakthrough after injecting about 5 PV of the 15 wt% solution.

Table 14- Core #B properties

Core #	L (cm)	D (cm)	Dry Wt. (gm)	Bulk Vol. (cc)	Sat. Wt. (gm)	Porosity (%)	Pore Vol. (cc)
B	4.247	3.751	97.83	46.93	108.7549	20.37	9.56

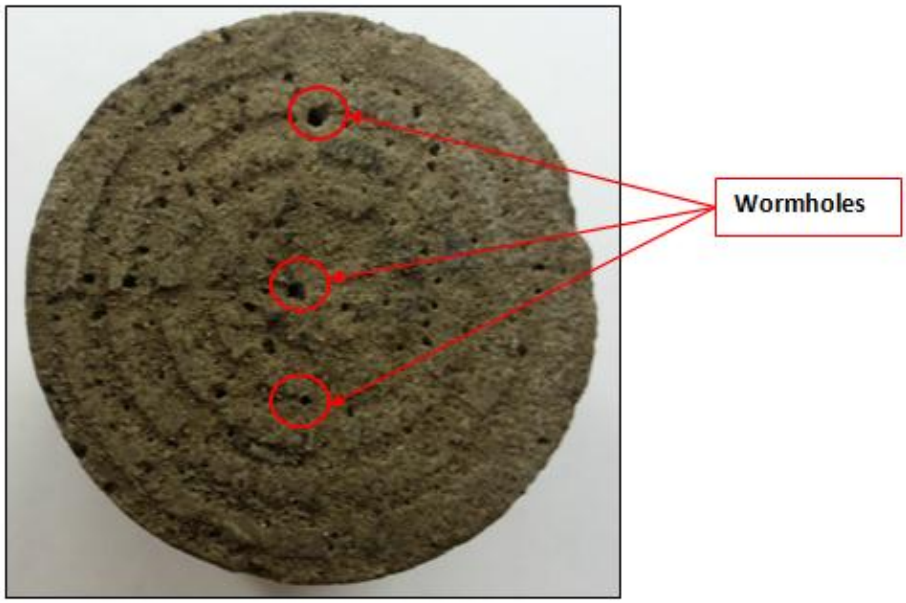


Fig. 40—Core #B Inlet after injecting about 8 PV of 15 wt% BCA solution at 0.5 cc/min.

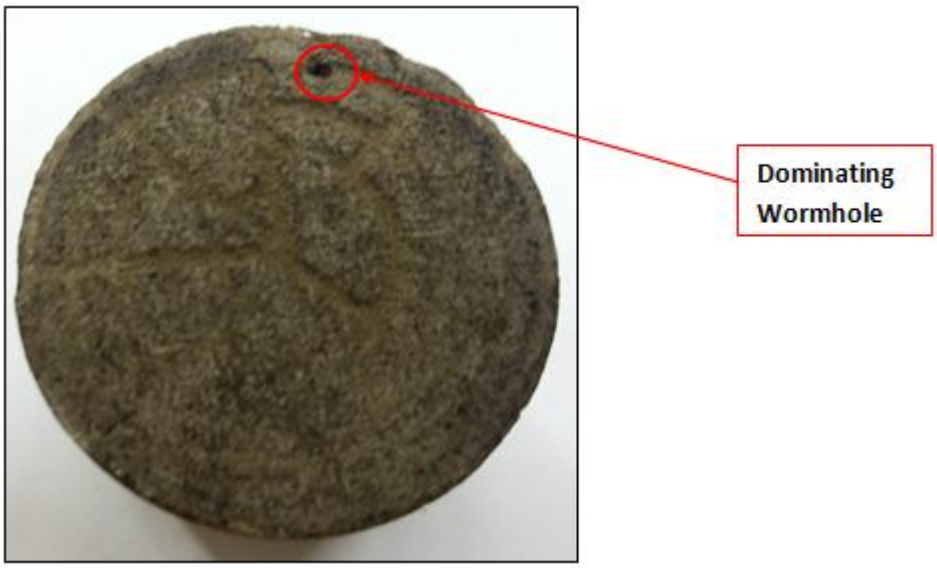


Fig. 41—Core #B Outlet after injecting about 8 PV of 15 wt% BCA solution at 0.5 cc/min.

Fig. 42—Coe #B after flooding with BCA/Gulf water solution showing core stability without any failure.

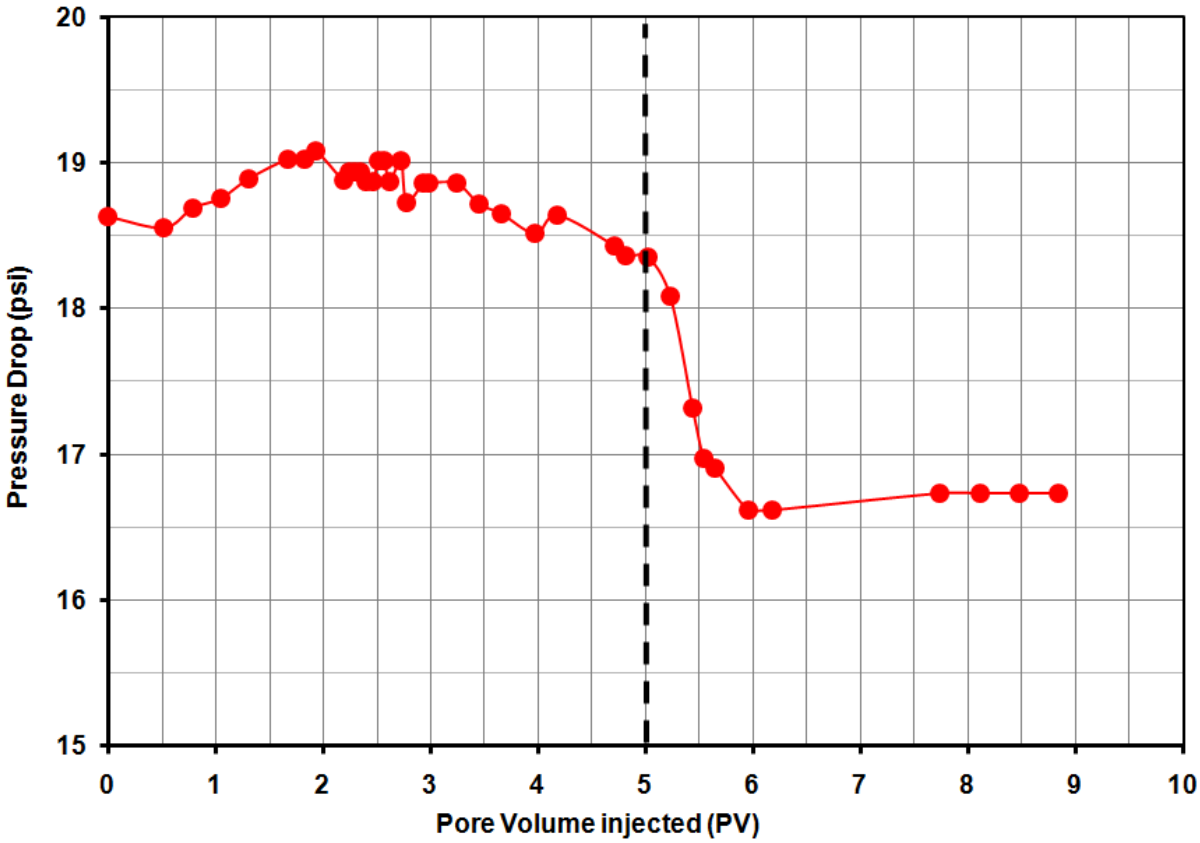


Fig. 43—Pressure drop during 15 wt% BCA/Gulf water solution injection at 0.5 cc/min, 1000 psi back pressure and 1500 psi overburden pressure

5.4 Conclusions

In this study extensive coreflooding tests have been performed to investigate the effect of using high pH EDTA chelating agents dissolved in Arabian Gulf seawater as a new innovative EOR technique. EDTA was shown to prevent formation damage during seawater injection into formation brine saturated core samples (either for EOR or pressure maintenance purposes). HEDAT and EDTA chelating agents were tested for in-situ CO_2 generated EOR method and they showed interesting results, however they were found to be incompatible with seawater. Low pH BCA was tested for compatibility with seawater and a stability test was performed to see its performance in the reservoir after being saturated with chelated cations. Based on the results of this study the following are the conclusions drawn from the study:

1. High pH chelating agents can be used as a cost effective EOR method in carbonate reservoirs compared to law salinity waterflooding and chemical EOR methods.
2. 20 % of the OOIP can be produced with the new EOR chelating agent method.
3. 5 wt% Na_4EDTA, NH_4EDTA should be used at with pH higher than 12 to have a significant recovery.
4. The IC analysis of the effluent showed that the additional oil recovery obtained could be attributed strongly to the rock dissolution which might make the recovery increase by LowSal waterflooding could be attributed to rock dissolution mechanism.
5. Out of the low pH chelating agents BCA is stable for in-situ CO_2 generation for EOR purposes at a concentration below 15 wt%, and other Low pH chelating are not compatible with seawater.

6. In-situ CO_2 generated by low pH chelating agents increased the recovery by 30% of the OOIP.
7. EDTA and HEDTA chelating agents at different concentrations were able to chelate all calcium from the solution and prevent the precipitation of calcium sulfate scales in limestone cores.
8. Increasing the concentration of HEDTA and EDTA resulted in chelating calcium from the rock matrix which enhances the rock permeability in limestone cores.
9. Low salinity water injection precipitated calcium sulfate in formation brine saturated core samples because of the low solubility of calcium sulfate at low salinity seawater.

5.5 Recommendations

Instead of injecting raw seawater for EOR or pressure maintenance in carbonate reservoirs, high pH EDTA can be added to the Arabian Gulf raw seawater for a cost effective EOR process. The industry has to look for new, cost effective and environment friendly low pH chelating agents compatible with seawater at a wide range of concentrations for EOR and in-situ CO_2 generation in carbonate reservoirs.

Appendix A

Table 15- Data for the recovery curve shown in Fig (15)

Injected Fluid	Injected PV	Produced Oil	Cumulative Oil Recovery (% OOIP)
Seawater	0	0	0
	0.384	4.17	33.74
	0.768	1.69	47.42
	1.153	0.45	51.07
	1.537	0.39	54.26
	1.921	0.20	55.86
	2.305	0.11	56.77
	2.689	0.12	57.77
	3.073	0.10	58.59
	3.458	0.06	59.05
	3.842	0.11	59.96
	4.226	0.15	61.15
	4.610	0.11	62.06
	4.994	0.11	62.97
	5.378	0.11	63.88
	5.763	0.06	64.34
	6.147	0.06	64.80
	6.531	0.06	65.25
	6.915	0.06	65.71
	7.299	0.06	66.16
	7.683	0.09	66.89
	8.068	0.08	67.58
	8.452	0.00	67.58
	8.836	0.02	67.71
	9.220	0.01	67.80
	9.604	0.01	67.85
	9.988	0.01	67.90
	10.373	0.01	67.99
	10.757	0.00	67.99
	11.141	0.00	67.99
	11.525	0.00	67.99
	11.909	0.00	67.99
	12.293	0.00	67.99
	12.678	0.00	67.99
	13.062	0.00	67.99

Table 16-Data for the IC shown in Fig (16)

PV	Sodium	Magnesium	Calcium	Chloride	Sulfate
1.15	23950	2080	2520	44701	4111
2.31	22652	2036	2161	43068	4211
3.46	21527	1990	1812	39326	4151
4.61	21258	2028	1641	38761	4293
5.76	20340	2006	1401	36691	4387
6.92	22301	1919	1482	36362	4337
8.07	26883	1635	1273	32682	4503
9.22	28319	1601	1286	28746	4301
10.37	28240	1606	1222	28267	4512
11.53	27762	1583	1211	28191	4557
12.68	27510	1552	1229	28798	4649
1.15	23950	2080	2520	44701	4111
2.31	22652	2036	2161	43068	4211
3.46	21527	1990	1812	39326	4151
4.61	21258	2028	1641	38761	4293
5.76	20340	2006	1401	36691	4387
6.92	22301	1919	1482	36362	4337
8.07	26883	1635	1273	32682	4503
9.22	28319	1601	1286	28746	4301
10.37	28240	1606	1222	28267	4512
11.53	27762	1583	1211	28191	4557
12.68	27510	1552	1229	28798	4649

Table 17- Data for the recovery curve shown in Fig (17)

Injected Fluid	Injected PV	Produced Oil	Cumulative Oil Recovery (% OOIP)
Seawater	0	0	0
	0.197	4.24	29.30
	0.394	2.34	45.46
	0.591	0.41	48.29
	0.789	0.29	50.31
	0.986	0.18	51.52
	1.183	0.18	52.73
	1.380	0.18	53.94
	1.577	0.12	54.75
	1.774	0.10	55.44
	1.971	0.12	56.25
	2.169	0.15	57.26
	2.366	0.13	58.19
	2.563	0.12	58.99
	2.760	0.09	59.64
	2.957	0.00	59.64
	3.154	0.00	59.64
EDTA/Seawater (3wt % EDTA)	3.4	0.05	59.99
	3.5	0.10	60.68
	3.7	0.15	61.71
	3.9	0.03	61.92
	4.1	0.05	62.27
	4.5	0.05	62.75
	4.7	0.06	63.17
	4.9	0.05	63.51
	5.1	0.08	64.06
	5.3	0.01	64.13
	5.5	0.01	64.22
	5.7	0.04	64.49
	6.1	0.01	65.11
	6.3	0.04	65.39
	6.5	0.01	65.46
	6.9	0.03	66.01
	7.1	0.02	66.15
	7.3	0.06	66.57
	7.7	0.00	66.57
	8.1	0.06	66.98
	8.5	0.00	66.98

Table 18- Cont. Data for the recovery curve shown in Fig (17)

Injected Fluid	Injected PV	Produced Oil	Cumulative Oil Recovery (% OOIP)
EDTA/Seawater (3 wt % EDTA)	8.9	0.02	67.12
	9.3	0.00	67.12
	9.7	0.04	67.39
	10.1	0.00	67.39
	10.4	0.00	67.39
	10.8	0.04	67.67
	11.2	0.02	67.81
	11.6	0.01	67.88
	12.0	0.05	68.22
	12.4	0.00	68.22
	12.8	0.01	68.29
	13.2	0.02	68.43
	13.6	0.02	68.57
	14.0	0.10	69.26
	14.4	0.06	69.68
	14.8	0.00	69.68
	15.2	0.00	69.68
	15.6	0.00	69.68

Table 19-Data for the IC shown in Fig (18)

PV	Sodium	Magnesium	Calcium	Chloride	Sulfate
0.591	28373	2213	3744	53866	4032
0.986	23906	2119	2417	44133	4211
1.380	22554	2109	1911	41241	4362
1.774	21379	2091	1601	38733	4395
2.169	20818	2063	1333	37459	4486
2.563	19905	2039	1108	35503	4487
2.957	19905	2064	1028	35156	4569
3.351	20231	2126	963	35871	4730
3.746	21923	1942	909	33034	4678
4.140	23491	1852	724	31918	4719
4.534	24188	1856	678	31740	4777
4.928	24115	1798	636	31149	4759
5.717	24373	1806	559	30676	4701
6.111	24908	1814	537	31300	4849
6.506	25035	1833	524	30887	4815
6.900	24856	1817	546	31049	4841
7.294	24460	1838	502	30649	4772
8.083	24662	1776	595	30643	4411
8.871	24857	1812	599	30874	4460
9.660	24623	1797	570	30551	4419
10.448	24656	1805	571	30399	4393
11.237	24641	1797	535	30405	4396
12.026	24558.5	1811	556	30552	4429
12.814	24973	1813	549	30842	4445
13.603	24548	1808	530	30126	4367
14.391	24658	1793	534	30393	4394

Table 20- Data for the recovery curve shown in Fig (19)

Injected Fluid	Injected PV	Produced Oil	Cumulative Oil Recovery (% OOIP)
Seawater	0.00	0.00	0.00
	0.43	5.73	39.32
	0.77	1.15	47.18
	1.11	0.52	50.72
	1.45	0.29	52.68
	1.79	0.23	54.25
	2.13	0.11	55.04
	2.47	0.20	56.42
	2.81	0.00	56.42
	3.15	0.00	56.42
EDTA/Seawater (5wt % EDTA)	3.44	0.10	57.10
	3.74	0.10	57.79
	4.04	0.20	59.16
	4.34	0.10	59.85
	4.64	0.20	61.22
	4.93	0.20	62.59
	5.23	0.22	64.10
	5.53	0.21	65.55
	6.12	0.17	67.95
	6.42	0.18	69.18
	6.72	0.18	70.42
	7.02	0.15	71.45
	7.31	0.15	72.48
	7.61	0.11	73.23
	7.91	0.13	74.12
	8.50	0.09	75.43
	8.80	0.05	75.77
	9.10	0.01	75.84
	9.40	0.02	75.98
	9.70	0.00	75.98
	9.99	0.02	76.08
	10.29	0.01	76.16
	10.59	0.02	76.30
	10.89	0.00	76.30
	11.18	0.02	76.44
	11.48	0.02	76.58
	11.78	0.00	76.58
	12.08	0.00	76.58

Table 21-Data for the IC shown in Fig (20)

PV	Sodium	Magnesium	Calcium	Chloride	Sulfate
1.11	26880	2140	3340	50625	3972
1.45	23950	2080	2520	44701	4111
1.79	22652	2036	2161	43068	4211
2.13	21527	1990	1812	39326	4151
3.15	21258	2028	1641	38761	4293
3.44	20340	2006	1401	36691	4387
3.74	22301	1919	1482	36362	4337
4.34	26883	1635	1273	32682	4503
4.93	28319	1601	1286	28746	4301
6.12	28240	1606	1222	28267	4512
6.72	27762	1583	1211	28191	4557
7.61	27510	1552	1229	28798	4649
8.21	29375	1660	1307	31392	4972
8.80	27647	1631	1258	30786	4737
9.10	27988	1596	1237	27846	4546
9.70	27752	1574	1196	27797	4511
10.29	28239	1618	1210	28136	4568
10.89	27829	1585	1202	27826	4518
11.48	26341	1512	1123	26288	4295
12.08	28437	1620	1208	28357	4542
12.67	27541	1566	1170	27476	4447
13.27	27811	1930	1181	27550	4443
13.86	28485	1611	1215	28216	4571
14.46	28310	1614	1214	28276	4552

Table 22- Data for the recovery curve shown in Fig (23)

Injected Fluid	Injected PV	Cumulative Oil Recovery (% OOIP)
Seawater	0	0
	0.05	1
	0.1	4
	0.15	6
	0.2	10
	0.25	11
	0.3	15
	0.35	17
	0.5	22
	0.55	26
	0.6	28
	0.65	30
	0.7	32
	0.85	35
	0.9	38
	0.95	40
	1	44
	1.05	48
	1.1	50
	1.15	52
	1.3	55
	1.35	56
	1.4	58
	1.45	58
	1.5	58
	1.55	58

Table 23- Cont. Data for the recovery curve shown in Fig (23)

Injected Fluid	Injected PV	Cumulative Oil Recovery (% OOIP)
Low pH HEDTA	1.65	60
	1.7	65
	1.75	66
	1.8	68
	1.85	72
	1.9	73
	1.95	75
	2	76
	2.05	78
	2.1	79
	2.15	80
	2.2	81
	2.25	82
	2.3	83
	2.35	85
	2.4	88
	2.45	90
	2.5	91
	2.55	92
Seawater	2.6	92
	2.65	92
	2.7	92
	2.75	92
	2.8	92
	2.85	92
	2.9	92
	2.95	92
	3	92
	3.05	92
	3.1	92

Table 24- Cont. Data for the recovery curve shown in Fig (24)

High pH EDTA (EOR#01)		Low pH EDTA (EOR#02)	
Injected PV	**Cumulative Oil Recovery (% OOIP)**	**Injected PV**	**Cumulative Oil Recovery (% OOIP)**
0	0	0	0.00
0.79	51.1	0.79	62.58
1.58	69.9	1.57	74.00
2.37	71.5	2.36	81.00
3.17	73.0	3.14	85.33
3.96	74.2	3.93	88.80
4.75	75.3	4.72	91.55
5.54	76.3	5.50	92.39
6.33	77.3	6.29	92.39
7.12	77.7	7.08	92.39
7.91	77.7	7.87	92.39
8.70	77.7	8.65	92.39
9.50	77.7	9.43	92.39
10.29	77.7	10.22	92.39

Table 25- Viscosity of UTMN dead oil at different temperatures (p=14.7 psi)

Temperature (^oC)	Viscosity (cp)
26.5	13.08
42.0	9.52
53.5	7.90
63.0	6.55
74.0	5.30
85.0	4.98
101.0	3.89

Table 26- Density of UTMN dead oil at different temperatures (p=14.7psi)

Temperature (^oC)	Density (gm/cc)
22.2	0.8756
35.6	0.8598
50	0.8472
65	0.8301
77	0.7948
103	0.7704

Table 27- pressure drop data shown in Fig. 34

Elapsed Time (min)	Injected (PV)	ΔP (psi)
0	0.00	20.06
5	0.47	20.05
7	0.66	20.32
10	0.95	20.45
12	1.14	20.38
15	1.42	20.31
17	1.61	20.59
20	1.90	20.52
22	2.09	20.59
25	2.37	20.45
27	2.56	20.86
30	2.85	20.86
32	3.04	20.86
35	3.32	20.58
37	3.51	19.75
38	3.61	19.47
39	3.70	19.34
40	3.80	18.99
41	3.89	18.85
42	3.99	18.64
43	4.08	18.02
44	4.18	17.74
45	4.27	17.26
46	4.37	16.98
47	4.46	16.98
48	4.56	16.98
49	4.65	16.98
50	4.75	16.98
51	4.84	16.98

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